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AN

INTRODUCTION

TO THE STUDY OF

ORGANIC CHEMISTRY.

BY

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TRANSLATED AND REVISED FROM THE FIFTH GERMAN EDITION

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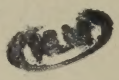
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PREFACE TO THE AMERICAN EDITION.

As a teacher of organic chemistry, I have felt the want of a small book on the subject. There is no lack of dictionaries and encyclopædic works on organic chemistry, but they are too large for use in a college course. The few shorter English text-books are not, so far as my experience goes, well suited for teaching.

The following work, which has met with remarkable success in Germany, and which the author, Prof. Pinner, has kindly given me permission to translate, is founded on the system of teaching developed by the distinguished chemist Prof. A. W. Hofmann, of Berlin, and in some cases follows his lectures quite closely.

The intention has been to make this book not a dictionary of compounds, or a work of reference for an investigator, but a *text-book* which can be placed in the hands of college students. It is believed that a student who has carefully studied and faithfully recited this book will be able to take up understandingly the larger works.

The retrospects at the end of each group afford the lecturer an opportunity of introducing a detailed recapitulation of the facts considered, as well as a survey of the typical reactions and theoretical relations of the various classes of substances. Coming in this place, such information is understood and appreciated by the student who has become acquainted with the compounds, and understanding the derivation of the individual members from each other, is prepared

to take up generalizations. But to begin with broad generalizations and the consideration of involved relations among groups of compounds with which the student is not acquainted, is hardly more rational than to undertake to teach the grammar of a language by lectures in that language to students who have not the slightest knowledge of its vocabulary or its inflections. The unfortunate manner in which the subject is so frequently taught, is probably the reason why organic chemistry is so often looked upon by students as a mere exercise for the memory, and a dry, unprofitable study.

In no other science has there been such remarkable development as in Organic Chemistry—the chemistry of the carbon compounds. Not so many years ago, Organic Chemistry was studied by but a few, and had but little practical importance. In fact, it was but little more than a description of a number of disconnected compounds, most of which occurred in plants and animals.

But within the last few decades, the increase of facts and compounds has been almost in a geometric ratio. It is no more a study of plant extracts or animal substances alone, but a science with fixed laws, and abounding in deductions and inductions, and including in its pursuit a remarkable discipline for the student's powers of reasoning as well as of comparison and judgment. The applications of Organic Chemistry form the foundation of some of the greatest manufactures existing, and its progress involves the prosperity of nations. Some of the greatest problems known to man are being slowly worked out by this science.

Instead of having but a few followers, it is not unsafe to say that more are devoting time to the study of this science than to any other. It seems to be the foundation of many of the other branches of study.

The explanation of the vital phenomena of animal and vegetable life—in fact, the whole subject of biology—the study of ferments and fermentation, the action of medicines, the

nature of the innumerable organic drugs, and the myriads of compounds whose effects have not yet been studied, make the study of this science a necessity to the druggist, physician, biologist and scientific man.

In many branches of manufacture the development of Organic Chemistry has been startling, and the field seems to be practically unlimited. The production of the brilliant aniline colors, alizarine and indigo, the fragrant oil of bitter almonds, and many valuable drugs from the waste tar of the gas works, seems to the uninitiated little short of the miraculous.

There is something wonderfully fascinating in the endless variations and permutations of the carbon compounds, the way in which, with a few atoms, the most complicated structures are built up or torn to pieces at the bidding of the chemist. There is hardly any other science, with perhaps the exception of electricity, that affords such a field for experimental investigation, invention and practical applications, and this, too, with the use of but little apparatus and at but a slight expense.

In this book the endeavor has been to explain the subject systematically, so that, with but a slight knowledge of chemical science, the student is able to advance easily to the most complicated compounds, and can at any place trace out the relationships of the particular compound to the simple ones from which it is derived. It is believed that this text-book will be found to be indispensable, not only to the professional chemist and student, but also to the physician, druggist and chemical manufacturer.

In translating Prof. Pinner's book, I have preserved so far as possible the easy lecture-style which is characteristic of it, and have not hesitated to employ numerous expressions which have come into use in working laboratories, and which recommend themselves for brevity and clearness.

So far as the limits of the book allow, I have introduced the more important recent discoveries in organic chemistry,

and have made free use of the literature and text-books at my disposal. In particular, I have to acknowledge my indebtedness to "Watt's Dictionary of Chemistry," the "Handwörterbuch der Chemie," the English edition of Wislicenus-Strecker, and the large work of Roscoe and Schorlemmer.

P. T. A.

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INTRODUCTION.

Ever since the composition of substances first began to be known, and to be used as a means of classification, compounds which contain carbon have been considered apart from those containing the other elements. This was partly because the number of the carbon compounds was so enormous, but chiefly because those which occur in nature were, with a few exceptions, produced by the vital processes of vegetable and animal life. All attempts to reproduce them from their elements failed. It was therefore supposed that it was impossible to produce them artificially, and that they were formed in *organic* nature by the influence of some mysterious force, which was called *vital* force. Hence the name, *organic chemistry*. Since that time multitudes of such substances have been produced from their elements, and the assumption of a vital force has long ago been given up, but the name remains in use. It is termed more correctly *the chemistry of the carbon compounds*.

The carbon compounds which occur in nature contain, besides carbon, only a few elements, viz., hydrogen, oxygen, and nitrogen. Some contain also sulphur and phosphorus. By chemical means, however, almost all the elements have been introduced into carbon compounds.

To understand the nature of a compound, it is necessary, first of all, to know of what elements it is composed, and in what relative amounts they are present. In studying organic compounds, therefore, the first step is to make a qualitative and quantitative analysis of them. As the methods

of qualitative and quantitative testing are usually the same, only the latter will be noticed here. The details of the operations will be given in the Appendix.

Carbon and hydrogen are always determined in one operation. A weighed amount of the substance is heated with an oxygen compound which gives up its oxygen easily at a high temperature, as cupric oxide or plumbic chromate. The carbon is oxidized to carbonic acid, and the hydrogen to water. This operation is called *combustion*. The water is absorbed in an apparatus containing fused calcium chloride, the carbonic acid in one filled with a solution of potassium hydroxide. By weighing the pieces of apparatus before and after the combustion, the weights of the water and carbonic acid absorbed are ascertained, and from them the the amounts of hydrogen and carbon are calculated.

Oxygen is not estimated directly, but is calculated as the difference between 100 per cent. and the sum of the per cents. of all the other constituents.

Nitrogen is estimated in two ways. (1.) By decomposing the substance in such a way that the nitrogen is given off as a gas. The gas is collected over mercury, and from its volume its weight is calculated, allowance being made for the temperature and pressure. (2.) The decomposition is so conducted that the nitrogen is converted into ammonia, the amount of which is estimated.

Chlorine, bromine, and iodine are combined with silver and estimated as silver chloride, bromide, or iodide, after destruction of the organic substance by ignition with caustic lime, or by oxidation at a high temperature with fuming nitric acid.

Sulphur and phosphorus are converted into sulphuric and phosphoric acids by oxidation of the organic substance (ignition with a mixture of potassium nitrate and sodium carbonate, or digestion with fuming nitric acid). The sulphuric acid is estimated as barium sulphate, the phosphoric acid as ammonio-magnesium phosphate.

When the relation of the amounts of all the constituents of an organic compound have been determined by the foregoing methods, the numbers representing the per cents. form the first step toward determining the chemical formula of the compound. If the number representing the per cent. of each element is divided by the atomic weight of the same, the relation of the elements to each other is obtained.

Suppose, for instance, a substance composed of carbon, hydrogen, and oxygen is found on analysis to contain 40 per cent. of carbon, 6.6 per cent. of hydrogen, and 53.4 per cent. of oxygen. Dividing by the atomic weights we have

$$C = \frac{40}{12} = 3.3$$

$$H = \frac{6.6}{1} = 6.6$$

$$O = \frac{53.4}{16} = 3.3$$

i.e., for every 3.3 atoms of carbon there are 6.6 atoms of hydrogen and 3.3 atoms of oxygen. It is at once evident that the relation of carbon to hydrogen and oxygen is 1 : 2 : 1. Hence the compound contains for one atom of carbon two atoms of hydrogen and one atom of oxygen, or CH_2O.

The formula thus obtained by no means expresses, in every case, the true chemical formula of the substance. It shows only the relation of the single atoms to each other. There is a great number of compounds in which the atomic ratio 1 C : 2 H : 1 O exists. One of them is a gas at ordinary temperatures, others are liquids, some are solids, and further, the liquids and solids differ greatly among themselves both in chemical and physical properties. But all of these compounds do not possess the same molecular weight, that is, all do not contain in a molecule only one atom of carbon, two atoms of hydrogen, and one atom of oxygen. In some cases a molecule contains two atoms of carbon, four atoms of hydrogen, and two atoms of oxygen, or double the simplest relation, in others treble, and so on.

Hence it becomes the task of the chemist, as soon as he has found out the percentage composition of a compound, and thereby ascertained the relation of the atoms to each other, to determine the molecular weight. There are various methods for doing this.

If the compound is a gas, or can by elevation of the temperature be brought into the state of a gas without decomposition, it is only necessary to determine the weight of a certain volume of the gas to ascertain the molecular weight; for, as is well known, the weights of equal volumes of different gases at the same temperature and same barometric pressure are in the same relation as their molecular weights, because equal volumes of gases always contain an equal number of molecules, no matter how different the gases may be. If, then, the weight of a volume of hydrogen is equal to two (since the weight of a molecule of hydrogen equals two), the weight of a volume of chlorhydric acid gas will be 36.5 (H = 1 + Cl = 35.5), or if we take a volume of hydrogen as equal to one, the weight of an equal volume of chlorhydric acid gas will be $\frac{36.5}{2} =$ 18.25. A volume of chlorhydric acid gas weighs, then, 18.25 times as much as an equal volume of hydrogen, weighed of course at the same temperature and pressure. Hence if we did not know what the molecular weight of chlorhydric acid was, but had found that it was 18.25 times heavier than hydrogen—in other words, we had estimated its weight by volume—it would only be necessary to multiply this volume-weight by two to obtain its molecular weight. The molecular weight of a substance is always twice as great as its volume-weight referred to hydrogen as unity. If we had, then, a substance, the simplest formula of which, according to analysis, was CH_2O, and it was found that its volume-weight = 30, we would know that its molecular weight would be $30 \times 2 = 60$. But the weight of a substance whose formula is expressed by CH_2O is $C + 2H + O = 12 + 2 + 16 = 30$. Hence the weight of our substance must be twice as great as CH_2O, that is, $2C + 4H + 2O = C_2H_4O_2$.

Let us assume we had found that a substance whose simplest formula was CH_2O, gave a volume-weight of 45. The

molecular weight would be $45 \times 2 = 90$, or three times as great as the formula CH_2O, that is $C_3H_6O_3$.

The methods of estimating the gaseous volume, or, as it is generally termed, the determination of the vapor density, of substances which are solid or liquid, at ordinary temperatures, will be described in the Appendix.

When the compound is a base or an acid, the molecular weight can be estimated by analyzing a salt of it and calculating the relation of the atoms to each other. Acetic acid, for instance, is a substance which has the atomic relation just mentioned, CH_2O. It is an acid and dissolves silver oxide, forming a crystalline compound, silver acetate, which contains

Carbon	= 14.4%	Oxygen	= 19.1%
Hydrogen	= 1.8%	Silver	= 64.7%

If these numbers are divided by the atomic weights of the corresponding elements, we have

$$C = \frac{14.4}{12} = 1.2 \qquad O = \frac{19.1}{16} = 1.2$$

$$H = \frac{1.8}{1} = 1.8 \qquad Ag = \frac{64.7}{108} = 0.6$$

We see at once that the relation of the silver to the carbon is as 1 : 2, to the hydrogen as 1 : 3, and to the oxygen as 1 : 2. Hence in this compound, for one atom of silver there are two atoms of carbon, three atoms of hydrogen, and two atoms of oxygen, or $AgC_2H_3O_2$. We know, however, that silver replaces one atom of hydrogen in acids. Replacing the atom of silver by an atom of hydrogen, we have $C_2H_4O_2$, which is the molecular formula of acetic acid. In a similar manner organic substances of a basic nature can be examined. Such bodies unite directly with acids, so that by determining the amount of acid with which they unite, the molecular weight of the compound can be calculated. If, on the other hand, the

substance is neither basic nor acid, and cannot be brought into the gaseous state without suffering decomposition, then only an accurate study of its chemical metamorphoses will lead to the determination of its molecular weight.

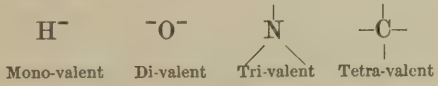
The formula which is deduced from the chemical composition and the molecular weight does not so characterize a substance that confusion with others is impossible. There is a great number of compounds which possess the same composition and molecular weight, but which differ greatly in chemical and physical properties. There are, for instance, five substances to whose composition and molecule the formula C_3H_6O corresponds. The differences between these five compounds can only arise from differences in their internal structure, or *constitution*. Whenever their relations do not show beyond a doubt which of the five substances is meant, it becomes necessary to express the structure, or constitution, in the formula. In this way, what are called constitutional (graphic, glyptic, structural) formulas have come into use.

To obtain a clear idea of constitutional or structural formulas, we must review certain laws which have already been mentioned in inorganic chemistry, but, owing to the simplicity of their relations in that branch of science, have not received the attention that they here require.

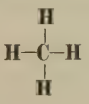
SUBSTITUTION.

Carbon is tetra-valent. Its tetra-valence and the replacement, or substitution, of the elements by each other in equivalent amounts, form the foundation on which the most complicated compounds are built up. The mono-valent hydrogen can be replaced atom by atom by the equally mono-valent chlorine, bromine, iodine, potassium, or silver. One atom of chlorine can take its position in the place of one atom of hydrogen. It occupies the same position as its predecessor, and the equi-valence, or equilibrium, of the compound, which has

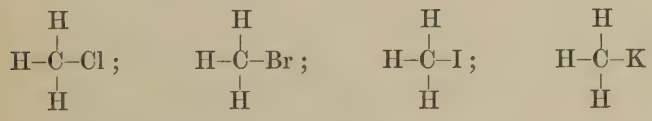
been disturbed by the exit of the atom of hydrogen, is restored by the introduction of the atom of chlorine, which has the same binding power, or valence, as the atom of hydrogen, being equal to one. An atom of hydrogen can also be substituted by an equi-valent amount of oxygen ; but since the atomic binding power of oxygen is twice as great as that of hydrogen, as seen in the compound H_2O, one atom of hydrogen could be replaced by only half an atom of oxygen. Half an atom of oxygen, however, cannot be imagined and does not exist, so we must say, more logically, that an atom of hydrogen can be substituted by half the atomic binding power of an atom of oxygen, in which case the other half must be kept in equilibrium by some other energy equal to that of the hydrogen, or one. To simplify matters, let us take up some illustrations. To represent the degree of the atomic binding power, or valence, we shall use a small stroke near the symbol. One stroke expresses unity.



The simplest carbon compound is composed of one atom of carbon and four atoms of hydrogen :

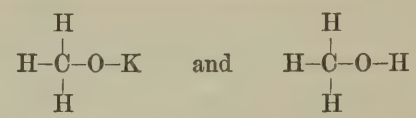


In this compound an atom of hydrogen can be substituted by an atom of chlorine, bromine, iodine, potassium, etc.

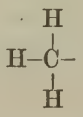


Again, an atom of hydrogen can be substituted by the half

of the atomic binding power of oxygen, the other half being satisfied by some other mono-valent atom, as

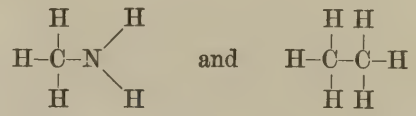


We see then that the group $^{-}O^{-}K$, or ^{-}OK, and $^{-}O^{-}H$, or ^{-}OH, can substitute an atom of hydrogen in the same manner as a mono-valent atom. It is not remarkable, therefore, that in the group CH_3 an unsatisfied bond, or valence, is free and active, and can only be rendered inactive by an equally great energy.



It makes no difference if this energy is the entire attractive power of a single atom of a mono-valent element, or the remainder of all the active attractive energies of an atomic group, so long as its amount is equal to one.

Proceeding in the same manner, an H can be substituted by the group NH_2 which is also mono-valent, or by the group CH_3:

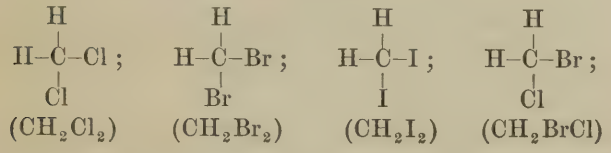


The last formula $CH_3{}^{-}CH_3$ brings us to a new carbon series, in which all the substitutions can be effected in the same manner as with the simple CH_4. We shall, however, continue with the first example, CH_4.

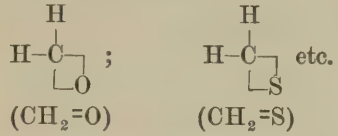
So far, only one atom of H, in the group CH_4, has been substituted by a mono-valent atom, or atomic group. In the same

manner, two atoms of H can be substituted by two mono-valent atoms, or atomic groups ; or by one di-valent atom, or atomic group.

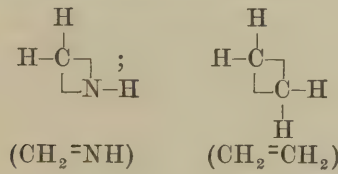
1) 2 H's by two mono-valent atoms :



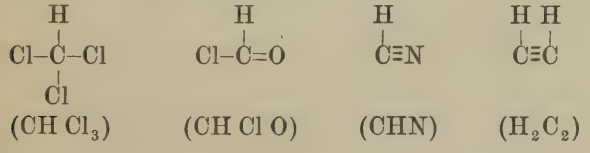
2) 2 H's by one di-valent atom :



3) 2 H's by one di-valent atomic group :



Further, three atoms of H in the CH_4 can be substituted by three mono-valent atoms, or atomic groups ; or by one mono-valent and one di-valent atom, or atomic group ; or by one tri-valent atom, or group.



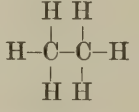
Finally all four of the H's can be substituted by four mono-valent atoms, or groups ; or by one di-valent and two mono-

valent atoms, or groups; or by two di-valent atoms, or groups; or by a tri-valent and a mono-valent atom, or group.

$C Cl_4$; $CO Cl_2$; CO_2 ; CN Cl.

We shall meet later a great number of substitutions. Here, however, it is only necessary to keep in view the principle that *only equi-valent amounts, or equal worths, of atoms can replace each other.*

Let us consider one of the examples just noticed, viz., the substitution of one of the atoms of H in the group CH_4 by the mono-valent group CH_3, or,

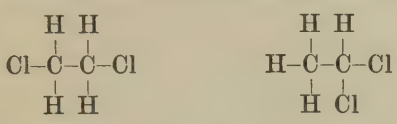


or $CH_3{}^-CH_3$, C_2H_6.

In this compound, which is more complicated than the preceding CH_4, the same substitutions can be effected as in the group CH_4. The number of the substitutions derived, however, will be greater. We shall also meet with substances which have the same composition, but totally different properties.

If in the group $CH_3{}^-CH_3$, an atom of H is substituted by a mono-valent atom, or atomic group (for the sake of simplicity we shall again choose chlorine), the compound $CH_3{}^-CH_2Cl$ is formed. There is but one such compound. It is immaterial whether we write $CH_3{}^-CH_2Cl$ or $CH_2Cl{}^-CH_3$, because the various atoms of hydrogen in the group $CH_3{}^-CH_3$ act in an entirely equal manner. No matter where the atom of chlorine is substituted, it occupies the same position in relation to the carbon and hydrogen in space. Hence there is only one compound possible which has the composition C_2H_5Cl or $CH_3{}^-CH_2Cl$. It is different, however, when a second H is substituted by a chlorine atom. There are now two cases possible. The second chlorine atom replaces an atom of

hydrogen belonging to the carbon atom which already possesses a chlorine atom, thus forming the compound $CH_3{-}CH\,Cl_2$, or it substitutes an atom of hydrogen belonging to the other carbon atom, and the compound $CH_2Cl{-}CH_2Cl$ arises. The relations are seen at once in the constitutional formulas:



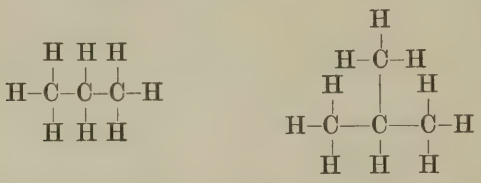
Here we have two compounds which have absolutely the same molecular weight, but yet must possess totally different properties because the different relative positions of the chlorine atoms influence the properties of the compound in a most marked manner.

Such compounds, possessing the same composition and molecule, but presenting differences in properties, are called *isomeric*. The great number of isomeric compounds has compelled the chemist to examine deeply into the structure or constitution of them; for, as has just been observed, in this case, only the dissimilarity of constitution can occasion differences in properties.

A similar case of isomerism presents itself when the group $CH_3{-}CH_3$ contains three chlorine atoms. It is seen at once that there are two modifications possible, $CH_2Cl{-}CH\,Cl_2$ and $CH_3{-}C\,Cl_3$. A third compound is not possible.

All the hydrogen atoms can successively be substituted by chlorine atoms or other elements, or atomic groups. The only other case that we shall examine, however, is the substitution of a hydrogen atom by the mono-valent atomic group CH_3, by which the compound $CH_3{-}CH_2{-}CH_3$ is obtained. If the same substitution be continued in this compound we shall obtain either $CH_3{-}CH_2{-}CH_2{-}CH_3$ or $CH_3{-}\underset{\displaystyle CH_3}{CH}{-}CH_3$, both C_4H_{10}. They are isomeric because in the one case the car-

bon atoms hang together like a chain, while in the other the three carbon atoms are bound to one :



By substitution of CH_3 in these two compounds we obtain,

1) $CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_3$;

2) $CH_3{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_3 = C_2H_5{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_3$;

3) $CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}CH_3$

All $= C_5H_{12}$.

In this case there are three isomers. With the compound C_6H_{14} the number will be much greater. With the increasing number of carbon atoms, the number of isomers increases with extraordinary rapidity according to the laws of permutations.

These compounds consisting only of carbon and hydrogen are called *hydrocarbons.* Placing them in a series, it is at once noticeable that each member differs from the preceding one by an increment of CH_2. If we represent the number of carbon atoms by n (n being any whole number from 1 on), then the number of H atoms is $2n + 2$. The series, therefore, possesses the general formula C_nH_{2n+2}. If we start out from the compound $CH_2{=}CH_2$, that is, one in which the carbon atoms are held together by two bonds, and substitute in this, as before, an atom of hydrogen by the group CH_3, we shall have $CH_2{=}CH{-}CH_3$, or C_3H_6. Continuing in the

same manner, we can substitute another hydrogen atom by a CH_3, obtaining $CH_2{=}CH{-}CH_2{-}CH_3$ and $CH_2{=}C(CH_3){-}CH_3$, both C_4H_8. Proceeding in this manner the following series is obtained :

$$C_2H_4\ ; \qquad C_3H_6\ ; \qquad C_4H_8\ ; \qquad C_5H_{10}.$$

These compounds have the general formula C_nH_{2n}, in which n denotes any whole number from 2 on. A body CH_2 is not known, and from the tetra-valence of carbon is not probable.

Two carbon atoms held together by three bonds give

$$CH{\equiv}CH, \text{ or } C_2H_2.$$

By substitution of this we get $CH{\equiv}C{-}CH_3 = C_3H_4$, so that another series of hydrocarbons can be built up, C_2H_2 ; C_3H_4 ; C_4H_6, etc., which fall under the general formula C_nH_{2n-2}, the smallest value of n being again 2.

Series of which each member is derived from the preceding member by the replacement of an H by a CH_3, are called *homologous.*

All compounds having the general formula C_nH_{2n}, C_nH_{2n-2}, etc., can be converted into those of the formula C_nH_{2n+2} ; that is to say, by the addition of hydrogen the double and treble binding of the carbon atoms can be broken until only the single binding remains. Hydrocarbons which are capable of taking up more hydrogen are termed *unsaturated,* or *unsatisfied* compounds. Those of the series C_nH_{2n+2}, not being able to take up any more hydrogen, are called *saturated* compounds.

$C_2H_4 = CH_2{=}CH_2$ can take up two more atoms of hydrogen, passing into $C_2H_6 = CH_3{-}CH_3$. In the same manner, $C_2H_2 = CH{\equiv}CH$ by combining with four atoms of hydrogen forms $C_2H_6 = CH_3{-}CH_3$.

We shall now proceed to the study of the individual organic compounds, taking up first those which contain only one atom of carbon, or derivatives of the hydrocarbon CH_4; then those containing two atoms of carbon linked together, or derivatives of the hydrocarbon C_2H_6; and after them the derivatives of C_3H_8, and so on.

C_1 GROUP.

Methane Compounds.

Methane, *Methyl Hydride, Marsh Gas, Fire-Damp ;* CH_4.

This compound, which is the simplest of the hydrocarbons, is found in marshes and coal mines (fire-damp). It is formed by the slow decomposition of organic substances in the absence of air. At some places it streams from the earth (at Baku); petroleum gases contain it. It is produced by the dry distillation of many organic substances, and forms an important constituent of illuminating gas.

Methane is made by heating a mixture of sodium acetate with an excess of sodium hydroxide :

$$\underset{\text{Sodium acetate}}{C_2H_3NaO_2} + NaOH = \underset{\text{Sodium carbonate}}{Na_2CO_3} + CH_4.$$

It can also be made synthetically by leading hydrogen sulphide and carbon disulphide over red-hot metallic copper :

$$\underset{\text{Carbon disulphide}}{CS_2} + 2\,H_2S + 4\,Cu_2 = CH_4 + 4\,\underset{\text{Cuprous sulphide}}{Cu_2S}.$$

It is a colorless and odorless gas, which condenses to a liquid at a very low temperature and under a very great pressure. The volume-weight of the gas = 8 (*i.e.*, it is eight times heavier than hydrogen). Its molecular weight = 16. It is easily combustible, burning with a scarcely luminous flame to carbonic acid and water. When mixed with air or oxygen it forms an explosive mixture :

$$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O.$$

This mixture constitutes the dangerous "fire-damp" of the coal mines, and has caused many frightful explosions when ignited by the miners' lamps. The introduction of the Davy safety-lamp has, however, greatly reduced the danger of its presence.

By exposing a mixture of equal volumes of methane and chlorine to diffused light, the first chlorine substitution of methane is obtained:

$$CH_4 + Cl_2 = CH_3Cl + HCl.$$

Halogen Substitutions.

I. One H of the Methane is substituted by a Halogen. (Alkyl-halogens, or Alkylogens.)

Methyl Chloride, *Chlormethyl, Mono-chlor-methane,* CH_3Cl, does not occur in nature. It is usually made by the action of nascent chlorhydric acid on methyl alcohol:

$$\underset{\text{Methyl alcohol}}{CH_4O} + H\,Cl = \underset{\text{Methyl chloride}}{CH_3Cl} + H_2O.$$

A mixture of methyl alcohol, salt, and sulphuric acid is heated, and the resulting product caught over water.

Colorless gas with a pleasant odor and sweet taste. Condenses in a freezing mixture to a liquid which boils at $-21°$. Vol. wgt. $= 25.25$. Mol. wgt. $= 50.5$.

Methyl Bromide, *Brom-methyl, Mono-brom-methane,* CH_3Br, is obtained from methyl alcohol and gaseous or nascent bromhydric acid:

$$CH_4O + H\,Br = CH_3Br + H_2O.$$

Bromine is allowed to drop into cooled methyl alcohol containing amorphous phosphorus.*

Colorless liquid with a pleasant odor, boiling at 5°. Vol. wgt. = 47.5. Mol. wgt. = 95.

Methyl Iodide, *Iodomethyl, Mono-iodo-methane,* CH_3I. From methyl alcohol and gaseous or nascent iodohydric acid.

$$CH_4O + HI = CH_3I + H_2O.$$

A solution of iodine in methyl iodide is added gradually to boiling methyl alcohol containing phosphorus.

Colorless liquid with a pleasant odor, boiling at 44°. Exposed to the light, it becomes yellow to red from a partial decomposition. Vol. wgt. = 71. Mol. wgt. = 142.

II. Two H's of the Methane are substituted by Halogens.

Methylene Chloride, Dichlormethane, CH_2Cl_2. It is formed, together with CH_3Cl, by the action of chlorine on methane. Also from chlorine on methyl chloride. But little known.

Methylene Bromide, Dibrom-methane, CH_2Br_2, and

Methylene Iodide, Di-iodo-methane, CH_2I_2.

As these three compounds are produced with difficulty, and have been as yet but little examined, they are only interesting as members of the series.

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* The compounds of phosphorus with chlorine, bromine, and iodine, PCl_3, PBr_3, PI_3, are decomposed by water into chlorhydric, bromhydric, and iodohydric acids.

$$PCl_3 + 3\,HOH = P(OH)_3 + 3\,HCl$$
$$PBr_3 + 3\,HOH = P(OH)_3 + 3\,HBr$$
$$PI_3 + 3\,HOH = P(OH)_3 + 3\,HI.$$

The alcohols act in exactly the same manner, except that the organic rests unite with the chlorine, bromine, or iodine. These reactions will be more fully considered later on.

Methylene iodide is made from iodoform by the action of strong iodohydric acid in presence of phosphorus :

$$CHI_3 + HI = CH_2I_2 + I_2.$$

Iodohydric acid sometimes substitutes retrogressively, *i.e.*, introduces hydrogen. Phosphorus is added to unite with the iodine as it becomes free, forming phosphorus tri-iodide, which, by decomposition with the water, yields fresh iodohydric acid.

III. Three H's of the Methane are substituted by Halogens. (Forms.)

Chloroform, *Trichlormethane,* $CHCl_3$, is also a product of the action of chlorine on methane :

$$CH_4 + 3\,Cl_2 = CHCl_3 + 3\,HCl.$$

It is made by the action of calcium hypochlorite (chloride of lime) on dilute alcohol.

1 part of chloride of lime, 4 parts of water, and $\frac{1}{8}$ part of alcohol of 0.85 sp. gr., are heated quickly until the reaction begins, and the heat then removed. Chloroform distils over mixed with water, from which it is afterwards separated, dried, and redistilled. The reaction takes place in two steps. By the action of chlorine on alcohol, chloral is first formed, but is decomposed into chloroform by the lime.

$$\underset{\text{Alcohol}}{C_2H_6O} + 4\,Cl_2 = \underset{\text{Chloral}}{C_2HCl_3O} + 5\,HCl.$$

$$2\,\underset{\text{Chloral}}{C_2HCl_3O} + Ca(OH)_2 = 2\,\underset{\text{Chloroform}}{CHCl_3} + \underset{\text{Calcium formate}}{Ca(CHO_2)_2}.$$

Chloroform is a colorless mobile liquid with a pleasant odor and sweet taste. Its specific gravity at 0° is 1.525, at 17°, 1.491. It boils at 62°. It burns difficultly, with a green-edged flame. It is very little soluble in water, but imparts its taste and odor to it. Easily soluble in alcohol and ether. When pure, it sinks in water without causing a troubling ; but if it contains alcohol, the water above remains troubled for a long time. By digestion with alcoholic potassium hydroxide it is decomposed into potassium formate and chloride :

$$CHCl_3 + 4\,KOH = \underset{\text{Potassium formate}}{CHO_2K} + 3\,KCl + 2\,H_2O.$$

Ammonia, in presence of potassium hydroxide, converts it into potassium cyanide and chloride:

$$CHCl_3 + NH_3 + 4\,KOH = \underset{\text{Potassium cyanide}}{KCN} + 3\,KCl + 4\,H_2O.$$

It is used in medicine as an anæsthetic. For this purpose it must be perfectly pure and dry. It must be clear and transparent, not troubled (moisture). It must have the correct specific gravity and boiling point (contamination with alcohol and foreign chlorides). It must not redden litmus paper or cloud a silver nitrate solution (free chlorhydric acid), and should give no precipitate of potassium chloride with an alcoholic potassa solution (foreign chlorides). For the production of chloroform for medicinal purposes, only a pure alcohol, free from fusel oil, should be used.

In the arts, chloroform is used as a solvent for bromine, iodine, alkaloids, phosphorus, rubber, resins, etc.

Bromoform, *Tri-brom-methane,* $CHBr_3$. Bromine is added to a solution of one part of potassium hydrate in one part of ethyl alcohol until a yellow color remains. The under layer of oil is bromoform.

It is a colorless liquid with an odor similar to that of chloroform. B. p. 152°. Sp. gr. at 12° = 2.9.

Iodoform, *Tri-iodo-methane,* CHI_3, two parts of sodium carbonate are dissolved in ten parts of water, and one part of alcohol is added, the whole warmed to 60–80°, and one part of iodine gradually added.

Yellow crystalline leaflets or tablets with an odor like saffron, fusing at 119°. It cannot be distilled in the dry state without partial decomposition. Quite easily soluble in alcohol and ether.

Its use in medicine depends on its large content of iodine. It acts like iodine, but more mildly.

IV. Four H's of the Methane are substituted by Halogens.

Carbon Tetrachloride, *Tetra-chlor-methane,* CCl_4.

Tetrachlormethane is the final product of the action of chlorine on methane, methyl chloride, and chloroform. It is usually made from the latter.

It is a colorless liquid with a pleasant odor, boiling at 78°. It is decomposed, by digestion with alcoholic potash, into potassium carbonate and chloride:

$$CCl_4 + 6\,KOH = K_2CO_3 + 4\,KCl + 3\,H_2O.$$

All of these chlorides, etc., when treated with nascent hydrogen, suffer a retrograde substitution, and yield methane. Sodium amalgam is a compound of mercury and sodium, which decomposes water slowly, giving a continuous evolution of hydrogen. If the chlorides, etc., are treated with sodium amalgam and water, methane will be obtained as the final product.

$$\begin{aligned} CH_3Cl &+ H_2 = CH_4 + HCl \\ CH_2Cl_2 &+ 2\,H_2 = CH_4 + 2\,HCl \\ CHCl_3 &+ 3\,H_2 = CH_4 + 3\,HCl \\ CCl_4 &+ 4\,H_2 = CH_4 + 4\,HCl. \end{aligned}$$

General reactions of the Chlorides, Bromides, and Iodides of the Hydrocarbons.

On account of the ease with which they exchange their halogen atoms for other mono-valent atoms, or atomic groups, the chlorides, bromides, and iodides of the hydrocarbons (alkylogens) serve as starting-out points for the production of other organic compounds. The study of them is hence very important.

(1) By digestion with sodium or potassium hydroxide, the halogen is substituted by OH, hydroxyl:

$$CH_3I + KOH = \underset{\text{Methyl alcohol}}{CH_3(OH)} + KI.$$

In the higher carbon series, potassic hydroxide generally splits out HCl, HBr, or HI from the alkylogens, and produces a hydrocarbon, or a derivative of a hydrocarbon, of the series C_nH_{2n}. This decomposition takes place particularly when one or more hydrogen atoms are substituted by halogens :

1) $CH_3{-}CH_2{-}CH_2I + KOH = KI + H_2O + CH_3{-}CH{=}CH_2$
or $CH_3{-}CH_2{-}CH_2I = HI + CH_3{-}CH{=}CH_2$
2) $CH_2Br{-}CH_2Br + KOH = KBr + H_2O + CHBr{=}CH_2$
$CH_2Br{-}CH_2Br + 2\,KOH = 2\,KBr + 2\,H_2O + CH{\equiv}CH.$

This procedure may be represented as taking place in two steps. In the first, the halogen is replaced by a hydroxyl group,

$$CH_2Br{-}CH_2Br + KOH = CH_2Br{-}CH^2(OH) + KBr,$$

this then combines immediately with a hydrogen atom of the neighboring carbon atom, thus occasioning the double binding of the carbon atoms :

$$CH_2Br{-}CH_2(OH) = CHBr{=}CH_2 + H_2O.$$

2) With potassium sulphhydrate, the halogen is substituted by SH, *sulphuryl :*

$$CH_3I + KSH = \underset{\text{Methyl-mercaptan}}{CH_3(SH)} + KI.$$

3) Ammonia effects the substitution of NH_2, *amidogen*, (amide, amine) for the halogen :

$$CH_3I + NH_3 = \underset{\text{Methylamine}}{CH_3(NH_2)} + HI.$$

4) With metallic zinc, the zinc compound of the hydrocarbon is formed :

$$2\,CH_3I + 2\,Zn = \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!Zn + ZnI_2.$$

5) With sodium alkoxide, the ethers are formed :

$$\underset{\text{Sodium methoxide}}{CH_3I + CH_3ONa} = \underset{\text{Methyl-ether}}{CH_3{-}O{-}CH_3} + NaI.$$

6) With the sodium or silver salts of the organic acids, the *esters*, compound ethers, or organic salts of the acids are produced :

$$\underset{}{CH_3I} + \underset{\text{Sodium formate}}{CHO_2Na} = \underset{\text{Formic methyl-ester}}{CH_3CHO^2} + NaI.$$

7) With potassium cyanide, the cyanides are formed :

$$CH_3I + KCN = CH_3(CN) + KI.$$

8) With potassium sulphocyanide, the sulphocyanides are produced :

$$CH_3I + KSCN = CH_3SCN + KI.$$

There is still a great number of reactions of which the alkylogens are capable, but the consideration of them would lead us beyond the limits of this work.

These reactions usually take place by treating the chlorides, etc., with potassium and silver compounds. The halogen and the metal unite, while the two rests combined to a new molecule. $XCl + YAg = AgCl + XY$.

The alkylogens are all very reactive, the order in activity being iodides, bromides, chlorides.

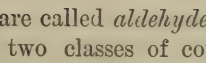
Hydroxyl Substitutions.

The hydroxyl substitutions of the hydrocarbons are the most important compounds in organic chemistry, because they are of the highest significance in the phenomena of life, and in the arts, and also yield the chemist the material from which all other derivatives are either directly or indirectly produced.

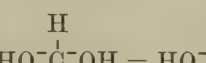
If an H in a hydrocarbon is replaced by a hydroxyl group (OH), an *alcohol*, or *carbinol*, is produced.

If 2 H's belonging to one carbon atom are replaced by 2 OH's, a molecule of H_2O splits off, and the remaining atom of O fills the gap.

$$CH_2(OH)_2 = CH_2O + H_2O$$



Such bodies are called *aldehydes,* or *ketones* (the difference between these two classes of compounds will be explained further on). If a third atom of H is substituted by OH, another molecule of water drops out, and a compound is formed having instead of three hydroxyls the group O (OH), as, for instance, CHO (OH).



Such compounds are called *acids.* The substitution of a fourth H by OH could only take place in the methyl group, as in all other series it is replaced by hydrocarbon rests. In the methane series, in this case, two molecules of water split off:

$$C(OH)_4 = CO_2 + 2\,H_2O.$$

Methyl Alcohol, *Carbinol, Wood Spirit, Methylated Spirit,* $CH_3(OH) = CH_4O$.

Methyl alcohol is produced with acetic acid in the distillation of wood. It occurs in combination with salicylic acid in the oil of wintergreen (*Gaultheria procumbens*).

It is obtained from the aqueous distillate of wood, or crude wood vinegar.

The product, which has been separated from the tar, is distilled over burnt lime several times down to about 10 %. Fused calcium chloride is then added. The crystalline compound of methyl alcohol and calcium chloride, which is obtained, is freed from all oily matters by washing with ether. Finally, the mass is distilled with water, which decomposes the compound. The methyl alcohol which is obtained in this manner, is

dehydrated by distillation over burnt lime, but is not chemically pure. For most purposes it is, however, sufficiently pure.

To obtain it absolutely pure, it is transformed into the crystalline oxalic ester, which is purified by repeated crystallizations, and distilled with water, which decomposes the compound. The aqueous alcohol thus obtained is freed from water by burnt lime and anhydrous cupric sulphate.

Methyl alcohol is a colorless, aqueous, mobile liquid, with an odor and taste like that of ordinary alcohol. B. p. = 65°. Sp. gr. at 0° = 0.798. Gas vol.-wgt. = 16, molecular wgt. = 32. It is soluble in all proportions in water, alcohol, ether, acetic acid, etc. Essential oils and all salts which are soluble in alcohol dissolve in it. It burns like alcohol.

In the arts it is used as a solvent (varnishes), in the manufacture of aniline colors, and for denaturalizing alcohol.

General Properties of the Alcohols (Carbinols.)

1) The alcohols on oxidation are converted into their corresponding aldehydes and acids. The mechanism of the reaction is as follows: A second, and then a third atom of hydrogen belonging to the same atom of carbon which holds the OH, is replaced by an OH, and in each case a molecule of water drops out:

$$CH_3OH + O = CH_2(OH)_2$$
$$CH_2(OH)_2 = \underset{\text{Aldehyde}}{CH_2O} + H_2O$$

further

$$CH_3(OH) + O_2 = CH(OH)_3$$
$$CH(OH)_3 = \underset{\text{Acid}}{CHO(OH)} + H_2O, \text{ or}$$
$$\underset{\text{Aldehyde}}{CH_2O} + O = \underset{\text{Acid}}{CHO(OH)}$$

2) All alcohols give with phosphorus trichloride, phosphorus tribromide, and phosphorus tri-iodide, the simple chlorides, bromides, and iodides of the hydrocarbons (alkylogens) and phosphorous acid. The reaction is the same as with water, and, in fact, the alcohols may be regarded as water in which

an H has been replaced by the mono-valent hydrocarbon rest. For example, methyl alcohol is methylated water :

$$\underset{\text{Water}}{H(OH)} \qquad \underset{\text{Methyl alcohol}}{CH_3(OH)}$$
$$3\,H(OH) + PCl_3 = 3\,HCl \quad + P(OH)_3$$
$$3\,CH_3(OH) + PCl_3 = 3\,CH_3Cl + P(OH)_3.$$

3) Alcohols dissolve sodium and potassium, forming solid compounds, which are very reactive, *i.e.*, the K or Na is easily exchanged for other mono-valent atoms, or groups. In this case, also, the alcohols act in the same manner as water :

$$HOH \quad + Na = \underset{\text{Sodium hydroxide}}{HONa} \quad + H$$
$$CH_3OH + Na = \underset{\text{Sodium methoxide}}{CH_3ONa} + H$$

4) With acids, the alcohols give up a molecule of water and form esters, or compound ethers (organic salts).* When acids possess several atoms of hydrogen substitutable by metals, are, in other words, polybasic, the resulting compounds, in which one or more of these replaceable H's are still present, are termed ester-acids.

$$CH_3(OH) + \underset{\text{Nitric acid}}{(HO)NO_2} = \underset{\substack{\text{Methyl nitric}\\ \text{ester}}}{CH_3ONO_2} + H_2O$$

$$CH_3(OH) + \begin{matrix}HO\\HO\end{matrix}\!\!\rangle SO_2 = \underset{\text{Sulphuric acid}}{\qquad} \qquad \underset{\substack{\text{Methyl sulphuric}\\ \text{acid}}}{\begin{matrix}CH_3O\\HO\end{matrix}\!\!\rangle SO_2} + H_2O$$

$$\begin{matrix}CH_3(OH) + HO\\CH_3(OH) + HO\end{matrix}\!\!\rangle SO_2 = \underset{\substack{\text{Methyl sulphuric}\\ \text{ester}}}{\begin{matrix}CH_3O\\CH_3O\end{matrix}\!\!\rangle SO_2} + 2\,H_2O$$

$$CH_3(OH) + \begin{matrix}HO\\HO\\HO\end{matrix}\!\!-PO = \underset{\text{Phosphoric acid}}{\qquad} \qquad \underset{\substack{\text{Methyl phosphoric}\\ \text{acid}}}{\begin{matrix}CH_3O\\HO\\HO\end{matrix}\!\!-PO} + H_2O$$

* It is better to consider them simply as salts, *e.g.*, methyl nitrate, etc.

$$\begin{matrix} CH_3(OH) \\ CH_3(OH) \end{matrix} + \begin{matrix} HO \\ HO \\ HO \end{matrix}\!\!>\!PO = \begin{matrix} CH_3O \\ CH_3O \\ HO \end{matrix}\!\!>\!PO + 2\,H_2O$$

Dimethyl-phosphoric acid

$$\begin{matrix} CH_3(OH) \\ CH_3(OH) \\ CH_3(OH) \end{matrix} + \begin{matrix} HO \\ HO \\ HO \end{matrix}\!\!>\!PO = \begin{matrix} CH_3O \\ CH_3O \\ CH_3O \end{matrix}\!\!>\!PO + 3\,H_2O$$

Methyl-phosphoric ester

With gaseous chlor- brom- or iodohydric acid, the alcohols yield, therefore, the chlorides, bromides, or iodides (alkylogens),

$$2\,CH_3(OH) + HCl = CH_3Cl + H_2O.$$

5) By warming with sulphuric acid, the alcohols yield their corresponding ethers,

$$2\,CH_3(OH) = \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!O + H_2O.$$

The term *ether* is given to those compounds which consist of two hydrocarbon rests united by an atom of oxygen, in other words, organic oxides.

Nearly all the reactions of the alcohols are easily explicable, when we assume that they behave in the same manner as the metallic hydroxides. For instance, methyl alcohol resembles KOH, potassium hydroxide.

1) The alcohols unite with the acids with loss of water to form esters. According to our assumption, then, these esters correspond to salts:

a) $CH_3HO + HONO_2 = \underset{\text{Methyl nitrate}}{CH_3ONO_2} + H_2O,$

$KHO + HONO_2 = \underset{\text{Potassium nitrate}}{KONO_2} + H_2O;$

b) $CH_3HO + HCl = CH_3Cl + H_2O,$

$KHO + HCl = KCl + H_2O;$

c) $CH_3HO + \begin{matrix} HO \\ HO \end{matrix}\!\!>\!SO_2 = \underset{\text{Primary methyl sulphate}}{\begin{matrix} CH_3O \\ HO \end{matrix}\!\!>\!SO_2} + H_2O,$

d) $2CH_3OH + \begin{matrix} HO \\ HO \end{matrix}\!\!>\!SO_2 = \underset{\text{Secondary methyl sulphate}}{\begin{matrix} CH_3O \\ CH_3O \end{matrix}\!\!>\!SO_2} + 2H_2O.$

With the polybasic acids, the alcohols form several series of salts. It is only when all the substitutable hydrogen atoms are replaced by alcohol (alkyl) rests, in our case, methyl, that the salt becomes neutral ; in all other cases the salts are acid, *i.e.*, they still contain hydrogen which can be substituted by a metal. The compound formed in equation c (primary methyl sulphate) is a monobasic acid, for it possesses one substitutable H which can be replaced by K, Na, etc., or by methyl, or any other alcohol (alkyl) rest.

In the esters, or compound ethers, as in the oxygen salts, the alkyl rest is bound by means of oxygen to the element forming the acid (linking function), in methyl nitrate with nitrogen, in methyl sulphate with the sulphur.

2) The alcohols pass into the ethers, that is, their oxides, exactly as the metallic hydroxides pass into the oxides :

$$CH_3OH + CH_3OH = \underset{\text{Methyl oxide}}{CH_3{}^-O{}^-CH_3} + H_2O$$

$$AgOH + AgOH = \underset{\text{Argentic oxide}}{Ag{}^-O{}^-Ag} + H_2O$$

It is by no means necessary that both of the affinities of oxygen should be neutralized by the same atomic group. The second bond may be satisfied by the atom of a metal as well as by any alkyl rest :

$$CH_3{}^-OH + Na = \underset{\substack{\text{Sodium}\\\text{methoxide}}}{CH_3{}^-O{}^-Na} + H \text{ analogous to}$$

$$K{}^-OH + Na = \underset{\substack{\text{Potassium so-}\\\text{dium oxide}}}{K{}^-O{}^-Na} + H$$

$$CH_3{}^-OH + C_2H_5{}^-OH = \underset{\text{Methyl-ethyl oxide}}{CH_3{}^-O{}^-C_2H_5} + H_2O$$

From these reactions we see that methyl alcohol behaves as a monovalent base. Later on we shall meet alcohols which deport themselves as di- and poly-valent bases.

Methyl alcohol dissolves sodium with considerable evolution of heat. The sodium substitutes an H of the hydroxyl :

$$CH_3OH + Na = CH_3ONa + H.$$

The resulting compound, CH_3ONa, sodium methoxide, is a solid. Water decomposes it into sodium hydroxide and methyl alcohol :

$$CH_3ONa + HOH = CH_3OH + NaOH$$

It yields the ether and sodium chloride with the chlorides, etc., of the alcohols (alkylogens) :

$$CH_3ONa + CH_3Cl = CH_3{}^-O{}^-CH_3 + NaCl.$$

Methyl alcohol, when treated with concentrated sulphuric acid, becomes highly heated, and the primary methyl sulphate, or methyl-sulphuric acid is formed, CH_3HSO_4. This acid forms salts with metals because it contains an atom of substitutable H. If the mixture of alcohol and acid is distilled, the neutral methyl sulphate, or methyl sulphuric ester is obtained, $(CH_3)_2SO_4$. If, however, there is not a great excess of sulphuric acid present (*e.g.*, when there is one part of alcohol to four of acid), *Methyl Oxide*, or *Methyl Ether* $(CH_3)_2O$, is formed. At ordinary temperatures it is a gas with a pleasant ethereal odor, becoming solid at $-$ 23°. It is very inflammable, and easily soluble in water.

All the ethers can be made in the same way as the methyl ether, either by heating the alcohol with concentrated sulphuric acid, whereby a molecule of water is removed. This amounts to the formation of an anhydride,

$$2\,CH_3OH = CH_3{}^-O{}^-CH_3 + H_2O.$$

Or by treating an alkylogen with the sodium compound of the alcohol (metallic alkyloxide) :

$$CH_3Cl + CH_3ONa = CH_3{}^-O{}^-CH_3 + NaCl.$$

Ethers with different hydrocarbon rests, or mixed ethers, can be produced by this later method.

Oxidation of Methyl Alcohol.

By leading the vapors of methyl alcohol mixed with air over a glowing platinum spiral, methyl aldehyde is formed. It is also produced by replacing both of the atoms of iodine in methylene iodide by an atom of oxygen. This is effected

by transforming the iodide into methylene acetate by treatment with silver acetate, and decomposing the acetate with potassic hydroxide,

$$CH_2I_2 + 2\ \underset{\text{Silver acetate}}{C_2H_3O_2Ag} = \underset{\text{Methylene acetate}}{CH_2(C_2H_3O_2)_2} + 2\ AgI.$$

$$CH_2(C_2H_3O_2)_2 + 2\ KOH = CH_2O + 2\ C_2H_3O_2K + H_2O.$$

Methylaldehyde, H^-CHO, or CH_2O. This aldehyde at ordinary temperatures is properly a gas. Its molecules possess the peculiar property, however, of uniting among themselves to form a complicated molecule, a body which, at ordinary temperatures, is solid, and fuses at 152°; at a higher temperature it is converted into vapor. This substance is called methyl-met-aldehyde. If it is brought into the gaseous state, it is decomposed into ordinary gaseous aldehyde. Such a fusion of several molecules is termed *polymerization.*

If the oxidation is effected by stronger agents, as, for instance, with manganic di-oxide and sulphuric acid, platinum black, or potassium dichromate and sulphuric acid, the trihydroxylated substitution-product is obtained :

$$CH_3(OH) + O_2 = CH(OH)_3 = \underset{\text{Formic acid}}{CHO(OH)} + H_2O.$$

The aldehyde, CH_2O, as above stated, is formed from methylene hydroxide, $CH_2(OH)_2$, by elimination of water (dehydration), since two hydroxyls cannot exist bound to the same carbon atom. If instead of hydroxyls, the group $^-O^-CH_3$ (methoxyl) be introduced, then stable compounds can be obtained having two, or even three, of these groups bound to one carbon atom.

Thus methylene iodide with potassium hydroxide gives (indirectly) methyl-aldehyde :

1) $CH_2I_2 + 2\ KOH = CH_2(OH)_2 + 2\ KI$;
2) $CH_2(OH)_2 = CH_2O + H_2O$.

Treated with potassium or sodium methoxide, however, it yields *Methylene Dimethoxide,* or *Methylal :*

$$CH_2I_2 + 2\ KOCH_3 = CH_2(OCH_3)_2 + 2\ KI.$$

Methylal can also be obtained by carefully oxidizing methyl alcohol with manganic di-oxide and sulphuric acid. It is a liquid with a pleasant odor, boiling at 42°, and soluble in 3 parts of water.

Formic Acid, $HCO(OH)$, CH_2O_2, occurs in nature. It exists in ants, in the needles of many pines, in nettles, etc. It is also a product of the decomposition of sugar, starch, gums, etc. In the animal organism it is contained in very small amounts in the blood and urine. It is formed by the oxidation of methyl alcohol; it is produced in the form of its potassium salt by the decomposition of iodoform, chloroform, and bromoform by means of potassium hydroxide; also from cyanhydric acid. Synthetically, it can be formed from carbonous oxide and potassium hydroxide.

Generally it is made by the decomposition of oxalic acid in the presence of glycerol. The oxalic acid falls into carbonic acid and formic acid:

$$\underset{\text{Oxalic acid}}{C_2H_2O_4} = CO_2 + CH_2O_2.$$

Equal parts of oxalic acid, dried at 100°, and glycerine are heated at 110° until the evolution of gas (carbonic acid) ceases; water is then added to the oily mass, and the whole distilled. In this way, a dilute acid is obtained. The pure acid is produced by the decomposition of its lead salt by hydrogen sulphide, plumbic sulphide and formic acid being obtained.

Formic acid is a colorless liquid with a penetrating odor and a strongly acid taste. It produces blisters on the skin. At 1° it solidifies to glittering crystals, which fuse at 8.6°, and boil at 99°. It is soluble in all proportions in water and alcohol. Its vapor is combustible. Owing to its tendency to become more highly oxidized, *i.e.*, to carbonic acid, it takes oxygen away from easily reducible substances, acting, therefore, as a reducing agent:

$$CH_2O_2 + O = CO_2 + H_2O.$$

It reduces, for instance, solutions of silver and mercury

salts. Concentrated sulphuric acid decomposes it into water and carbonous oxide :

$$CH_2O_2 = CO + H_2O.$$

When heated with water formic acid forms a hydrate, $CH_2O_2 + H_2O$, or $CH(OH)_3$, *Orthoformic acid*, which boils at about 106°.

General Remarks on the Organic Acids.

Formic acid may be considered as the prototype of all organic acids. When we examine its constitution we find that the four valences of the carbon are satisfied in the following manner :

One valence by an H,
Two valences by an O, and
One valence by the group OH ;

$$O=\overset{H}{\overset{|}{C}}-O-H.$$

The atom of H, which is united to the carbon, can be substituted by any mono-valent organic group. The group may be a very complicated one, the only condition being that it must possess *one* free valence. On the other hand, the group COOH, which in formic acid is bound to an atom of H, can enter an organic compound as a mono-valent group, and form an acid. The group COOH is called *carboxyl*, and acids formed by its introduction are known as *carboxylic acids.* The hydrogen of the carboxyl group acts as the hydrogen of inorganic acids, being easily substituted by metals. It is the so-called *basic hydrogen.* As the carboxyl group contains only one atom of replaceable hydrogen, it is *monobasic.* Organic acids which contain only one carboxyl group are therefore *monobasic acids.*

If an organic acid contains two carboxyl groups, it is dibasic, etc. The number of carboxyl groups determines the

degree of basicity. Two simple examples will serve to illustrate this. If, in formic acid, the atom of hydrogen which is bound to the carbon atom is replaced by the methyl group, CH_3, the compound $CH_3{}^-COOH$ (or $C_2H_4O_2$), acetic acid, is formed. Acetic acid is a monobasic acid because it contains but *one* carboxyl group. If, on the other hand, the same atom of hydrogen is replaced by a carboxyl group, the compound

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \text{ (or } C_2H_2O_4\text{), oxalic acid,}$$

is formed. Oxalic acid is a dibasic acid because it contains *two* carboxyl groups.

On comparing the empirical composition of formic acid with that of methyl alcohol, it will be found that it contains two atoms of hydrogen less, and one atom of oxygen more, than methyl alcohol. *All acids contain two atoms of hydrogen less, and one atom of oxygen more, than the alcohols from which they are derived.*

The laws of substitution which have been mentioned find application in the acids.

1) The hydrogen of the carboxyl can be substituted by a metal forming a salt, as H^-COONa, sodium formate.

2) The hydrogen of the carboxyl can be substituted by alcohol (alkyl) rests, forming esters, compound ethers, or organic salts :

$$H^-COO^-(CH_3)$$ Methyl-formic ester.

3) The hydrogen of the carboxyl can also be replaced by an acid rest. An acid rest is an acid less OH. The rest of formic acid is CHO :

$$H^-CO(OH) + H^-CO(OH) = H^-CO.O.HCO + H_2O.$$

Compounds formed in this manner are called *anhydrides.*

Their constitution is analogous to that of the inorganic acid anhydrides :

$$\underset{\text{Nitric acid}}{NO_2(OH)} + NO_2(OH) = \underset{\text{Nitric anhydride}}{NO_2{}^-O^-NO_2} + H_2O$$

$$\underset{\text{Formic acid}}{CHO(OH)} + CHO(OH) = \underset{\text{Formic anhydride}}{CHO^-O^-CHO} + H_2O.$$

As the anhydride of formic acid is not yet known, this class of compounds will be considered under the next acid, acetic acid.

4) The hydroxl of the carboxyl can be replaced by Cl.

This derivative of formic acid, which would have the formula H^-COCl, has not yet been obtained, because it decomposes at once into CO and HCl, but the reaction takes place with almost all the other acids.

The compounds thus obtained are called *aci-chlorides*. The chlorine in them is remarkably easy of substitution by other mono-valent atoms, or atomic groups. They are decomposed by water, the hydroxl taking the place of the chlorine :

$$\underset{\text{Acetyl chloride}}{CH_3{}^-CO^-Cl} + H_2O = \underset{\text{Acetic acid}}{CH_3{}^-CO^-OH} + HCl.$$

Ammonia affects the substitution of the Cl by NH_2 :

$$CH_3{}^-CO^-Cl + NH_3 = CH_3{}^-CO^-NH_2 + HCl.$$

5) The hydroxyl of the carboxyl can be substituted by the group NH_2, $H^-CO^-NH_2$, Formamide.

6) By distillation of the salt of an organic acid with an excess of alkali, the carboxyl group is split off and replaced by H :

$$\underset{\text{Sodium formate}}{H^-COONa} + NaOH = HH + \underset{\text{Sodium carbonate}}{Na_2CO_3}$$

$$\underset{\text{Sodium acetate}}{CH_3{}^-COONa} + NaOH = \underset{\text{Methane}}{CH_4} + Na_2CO_3.$$

7) By the distillation of an organic salt by itself, a carbonate is also formed, two molecules of the acid acting on each other. But, in this case, the two acids rest unite. We shall

examine this reaction more carefully later on. From formic acid, methyl aldehyde is produced :

$$\underset{\text{Sodium formate}}{H^-COONa} + H^-COONa = Na_2CO_3 + \underset{\text{Methylaldehyde}}{CH_2O}.$$

There are also various other reactions which we shall have occasion to study.

Among the salts of formic acid which are worthy of notice are the sodium salt, HCOONa; the lead salt $(HCOO)_2Pb$, from which the pure acid is obtained ; and the ammonium salt, $HCOONH_4$, which by rapid heating falls into cyanhydric acid and water :

$$HCOONH_4 = HCN + 2\,H_2O.$$

Formic acid is properly an anhydride acid formed from $CH(OH)_3$ by elimination of water. Although the salts of this acid, the orthoformic acid, have not been produced, its esters are known. By the action of sodium methoxide on chloroform, the orthoformic methyl ester is produced, while by the action of sodium hydroxide on chloroform, only the ordinary formic acid is formed :

$$CHCl_3 + 3\,NaOCH_3 = CH(OCH_3)_3 + 3\,NaCl,$$
$$CHCl_3 + 3\,NaOH \quad = CH(OH)_3 \quad + 3\,NaCl,$$
$$CH(OH)_3 = CHO(OH) + H_2O.$$

The final hydroxyl substitution-product of methane, into which formic acid has such a tendency to pass, is $C(OH)_4$. As soon as this body enters the free state, two molecules of water are eliminated, so that the compound CO_2 is formed. ($CH_4O_4 - 2\,H_2O = CO_2$.) If, however, it does not pass into the free state, but at least one atom of hydrogen is replaced by a metal, or hydrocarbon rest, the molecule of water is not split off, and a derivative of the compound $CO(OH)_2$ or CH_2O_3 is formed.

The compound $C(OCH_3)_4$, *Orthocarbonic Methylester*, how-

ever, is stable, and can be obtained by the action of sodium methoxide on carbon tetrachloride :

$$CCl_4 + 4\,NaOCH_3 = C(OCH_3)_4 + 4\,NaCl.$$

By the action of sodium hydroxide on carbon tetrachloride, however, besides sodium chloride, only sodium carbonate is produced.

Carbonic Acid, CO_2. This acid and its salts have already been studied in inorganic chemistry.

Substitution products of carbonic acid. Both hydroxyls of the hypothetical carbonic acid, $CO(OH)_2$, are replaced by chlorine.

Chlorcarbonous oxide, phosgen, chlorcarbonyl, $COCl_2$, is formed by the union of chlorine and carbonous oxide in sunlight. It is a colorless gas with an unpleasant odor, which condenses in a freezing mixture to a liquid boiling at 8°. With water it is decomposed into carbonic acid and chlorhydric acid :

$$COCl_2 + H_2O = CO_2 + 2\,HCl.$$

Chlorcarbonous oxide being the chloride of carbonic acid, is an aci-chloride, and possesses all the properties mentioned as belonging to that class of compounds. If chlorcarbonyl is conducted into an alcohol, the corresponding chlorcarbonic ester is obtained :

$$COCl_2 + CH_3OH = HCl + CO\begin{cases} OCH_3 \\ Cl \end{cases}$$

Chlorcarbonic methylester

The chlorcarbonic esters exchange their chlorine very easily for other atoms, or atomic groups, and are often used as a means of introducing the carboxyl group into compounds.

Sulpho-Substitution-Products of Methane.

There are sulpho-derivatives containing sulphur in place of the oxygen, which correspond to most of the oxygen derivatives of methane.

Methyl sulphydrate, or methyl mercaptan, CH_3SH, corresponding to the methyl alcohol, CH_3OH, is a colorless liquid with a most unpleasant odor, boiling at 21°. The mercaptans give with mercuric oxide a white crystalline compound, from which their name* is derived. They are produced by the action of potassium, or sodium sulphydrate, on the alkylogens.

Methyl sulphide, $(CH_3)_2S$, corresponding to methyl ether, is a liquid with an unpleasant odor, boiling at 41°. Its production is analogous to that of the sulphydrates, but instead of the sulphydrate the sulphide is used.

Methyl sulphaldehyde, CH_2S, corresponding to methyl aldehyde. It polymerizes to three molecules, so that its proper formula is $C_3H_6S_3$. It is obtained by the reduction of carbon disulphide.

Carbon Disulphide, CS_2, corresponding to carbonic acid, CO_2. It is formed when sulphur vapors are led over glowing coals. A colorless liquid, very refractive, with an unpleasant odor and a sharp taste, boiling at 46°. Its sp. gr. is 1.27. It is easily inflammable, burning with a blue flame to carbonic and sulphurous anhydrides :

$$CS_2 + 3\,O_2 = CO_2 + 2\,SO_2.$$

It is insoluble in water, and miscible with alcohol, ether, fatty and essential oils. It dissolves bromine, iodine, sulphur, phosphorus, fats, etc.

In the arts is considerably used as a solvent (extraction of oils, fats, and sulphur). It is also used in medicine.

Nascent hydrogen converts it into methyl sulphaldehyde :

$$CS_2 + 2\,H_2 = CH_2S + H_2S.$$

Between carbon disulphide and carbonic acid there stands a

* "Corpus Mercurio Aptum."

compound, COS, *Carbon Oxysulphide.* It is a colorless gas, and is produced by the action of very concentrated acids (sulphuric, acetic), on potassium sulphocyanide. It is easily inflammable and is converted gradually by water, quickly by bases, into carbonic acid and hydric sulphide :

$$COS + H_2O = CO_2 + H_2S.$$

Corresponding to the numerous salts (carbonates) and derivatives of carbonic acid, there are salts and derivatives of carbon disulphide. Carbonic acid in the free state appears always in the form of an anhydride, but considered in relation to its derivatives it has the formula $CO(OH)_2$. In the same manner, the carbon disulphide must be considered as an anhydride when in the free state. There are deduced from the latter two series of compounds, depending on whether the primary type is $CS\langle^{SH}_{SH}$ or $CS\langle^{S\,H}_{OH}$. Finally there is a third, which stands nearer the carbonic acid derivatives than the second, $CO\langle^{S\,H}_{OH}$. We have then :

$CS\langle^{S\,H}_{S\,H}$, trisulphocarbonic acid series.

$CS\langle^{S\,H}_{OH}$, disulphocarbonic acid series.

$CO\langle^{S\,H}_{OH}$, monosulphocarbonic acid series.

With the latter two series there are two isomers :

$CO\langle^{S\,H}_{S\,H}$, isodisulphocarbonic acid series.

$CS\langle^{OH}_{OH}$, isomonosulphocarbonic acid series.

Chiefly the salts and ethers of these series are known ; *e.g.*,

$CS\langle^{SCH_3}_{SCH_3}$, trisulphocarbonic methylether.

a) The potassium salt of the first series is produced by mixing carbon disulphide with a solution of potassium sulphide:

$$CS_2 + K_2S = K_2CS_3.$$ Potassium trisulphocarbonate.

The ethers can be easily obtained from these salts by the action of the alkylogens.

b) The potassium salt of the second series is obtained by mixing carbon disulphide with potassium hydroxide solution:

$$CS_2 + 2\,KOH = H_2O + K_2CS_2O.$$ Potassium disulphocarbonate.

If, instead of an aqueous solution of potassic hydroxide, the alcoholic solution is used, the methyl-ethyl, etc., salt of the disulphocarbonic acid is obtained, depending on the alcohol taken. By using methyl alcohol, for instance, the compound $CS\langle^{SK}_{OCH_3}$ is formed.

$$CS_2 + KHO + CH_3HO = K(CH_3)CS_2O + H_2O.$$

These compounds are known as *xanthic acid* compounds. The one given is potassium methylxanthate. From the xanthic acid salts, the esters may be produced by the usual methods.

c) The esters of the third series are produced by the action of chlorcarbonic ester ($CO\langle^{OCH_3}_{Cl}$) on the potassium compound of the mercaptans:

$$CO\langle^{OCH_3}_{Cl} + CH_3SK = CO\langle^{OCH_3}_{SCH_3} + KCl.$$

Chlorcarbonic-methyl ester — Potassium methyl mercaptid — Methylmono-sulphocarbonate

d) The esters of the fourth series are obtained by the decomposition of the sulphocyanic ethers (see later) with concentrated sulphuric acid.

e) The esters of the fifth series are produced by the decomposition of the xanthic esters by means of alcoholic potassa:

$$CS\langle^{SCH_3}_{OCH_3} + KOH = CS\langle^{OCH_3}_{OK} + CH_3SH.$$

Methyl xanthogenate

The only free acids which are known are *sulphocarbonic acid*, H_2CS_3, $CS\langle^{SH}_{SH}$, a reddish-brown unstable oil, and *disulphocarbonic acid*, H_2CS_2O, $CS\langle^{S\,H}_{OH}$, a compound existing only at very low temperatures.

Sulphocarbonyl chloride, carbon sulphochloride, $CSCl_2$, corresponding

to carbonyl chloride, $COCl_2$, is obtained by the action of chlorine on carbon disulphide. It is a reddish liquid with a suffocating odor, boiling at 70°. It polymerizes gradually when exposed to the light, and changes into colorless crystals melting at 112°.

Finally, a series of sulphur derivatives must be mentioned which have the same composition as the primary esters of sulphurous acid, but are distinguished from them by the sulphur being bound directly to the carbon, while in the others it is bound through oxygen. They are called *sulphonic acids*, and form crystalline salts soluble in water.

As sulphurous acid has the constitution $SO_2\langle^{OH}_{H}$, there are two monomethyl derivatives possible The first is $SO_2\langle^{OCH_3}_{H}$, primary methyl sulphite, or methyl sulphurous acid, and is an ester, or compound ether, because the methyl is bound to the sulphur by means of oxygen. The other is $SO_2\langle^{OH}_{CH_3}$, methylsulphonic acid.

In the latter, the hydroxyl group of sulphuric acid is replaced by a hydrocarbon rest.

They are produced by digesting the chlorides, bromides, or iodides of the hydrocarbons with neutral ammonium sulphite:

$$CH_3I + (NH_4)_2SO_3 = CH_3SO_3NH_4 + NH_4I,$$

or by oxidizing the mercaptans with nitric acid,

$$CH_3SH + O_3 = CH_3SO_3H.$$

Methylsulphonic acid, CH_3SO_3H, and *Methylene-sulphonic acid*, $CH_2(SO_3H)_2$, are known in the pure state only in the form of their salts.

By the oxidation of methyl sulphide, *Methylsulphone*, $(CH_3)_2SO_2$, is obtained. It has the constitution,

$$O\!\!>\!\!S\langle^{CH_3}_{CH_3}$$

We shall examine the sulpho-acids more thoroughly when we come to the aromatic compounds, for their sulphonic acids are of much greater importance.

Nitrogen Substitution Products of Methane.

Next to the oxygen derivatives of the hydrocarbons, the nitrogen derivatives are the most important, even surpassing them in variety. Nitrogen as a tri-valent element can substitute three hydrogen atoms in one or more hydrocarbons; in combination with H (as $NH^{=}$), it can substitute two atoms of H in one or more hydrocarbons; and, finally, in combination with two H's (NH_2^{-}), it can substitute one H atom in a hydrocarbon.

It is evident that in these substituted hydrocarbons other substitutions may exist, hydroxyl in place of hydrogen, for instance; as examples we have:

1) Substitution of 1 N for 3 H's in a hydrocarbon:

a) $CH{\equiv}N$; b) $C(OH){\equiv}N$;

2) Substitution of NH for two H's:

a) $CH_2{=}NH$; b) $CO{=}NH$;

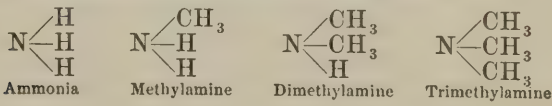
3) Substitution of NH_2 for H:

a) $CH_3{-}NH_2$; b) $CHO{-}NH_2$.

This class of compounds is more easily understood when we look at them from another point of view, that is, as derived from ammonia.

In ammonia the three H's can be successively substituted:

1) By mono-valent hydrocarbon rests (alkyl rests):



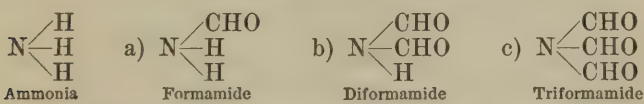
These bodies are called *amines*, or *amine bases*. They resemble ammonia in every way, possess basic properties, unite directly with acids, as, for instance,

NH_3HCl, ammonium chloride;
$NH_2(CH_3)HCl$, methylammonium chloride;
$NH(CH_3)_2HCl$, dimethylammonium chloride;
$N(CH_3)_3HCl$, trimethylammonium chloride.

It is even possible in these compounds to substitute the H of the acid by an alkyl rest, thus obtaining compounds such as $N(CH_3)_4Cl$, tetramethylammonium chloride. In this last compound the chlorine, or halogen, atom can be replaced by hydroxyl, forming the compound $N(CH_3)_4OH$, tetramethylammonium hydroxide.

Ammonia dissolved in water has also the formula $NH_4(OH)$, ammonium hydroxide, but such a compound cannot be isolated, because it falls at once into water and ammonia, $NH_4(OH) = NH_3 + H_2O$. If, however, the four H's of the ammonium hydroxide be substituted by alkyl rests (methyl), the compound becomes stable and can be isolated.

2) The hydrogen of the ammonia can be successively substituted by mono-valent acid rests. The hydroxyl of formic acid, HCO(OH), can, for instance, be replaced by NH_2:



These compounds are called *amides*. The last two have not yet been produced in the case of formic acid, but we shall meet them under acetic acid. The first amide still possesses weak basic properties; for by the entrance of the acid rest the attraction of the ammonia for acids is almost neutralized.

Amines are, then, substituted ammonias, in which the hydrogen is replaced by hydrocarbon rests, or, when we imagine the hydroxyl to be replaced by the amido-group, by alcohol rests. Amides are substituted ammonias in which the hydrogen is replaced by acid rests.

$CH_3(OH)$	$CH_3(NH_2)$
Methyl alcohol	Methylamine
$HCO(OH)$	$HCO(NH_2)$.
Formic acid	Formamide

The group NH_2 is known as *amidogen*, or the *amido-group;* NH, as *imidogen*, or the *imido-group.*

If the organic rest combined with NH_2 contains another carboxyl group, as is the case when in dicarboxylic acids only one of the carboxyl groups exchanges its hydroxyl for NH_2, compounds arise which have a weak acid character; for the introduction of the NH_2 has not the power to entirely overcome the acid properties. Such compounds are called *amido-acids* or *amic acids.* In the compound $\begin{matrix}CO(OH)\\CO(OH)\end{matrix}$, oxalic acid, for instance, one or both of the hydroxyls may be substituted by the NH_2 group. In the first case an amido-acid $\begin{matrix}CO^-NH_2\\CO^-OH\end{matrix}$ is formed; in the second, an amide $\begin{matrix}CO^-NH_2\\CO^-NH_2\end{matrix}$. In fact, the hypothetical carbonic acid $CO\langle\begin{matrix}OH\\OH\end{matrix}$ yields two such compounds, $CO\langle\begin{matrix}NH_2\\OH\end{matrix}$, amidocarbonic acid (carbamic acid, amidoformic acid), and $CO\langle\begin{matrix}NH_2\\NH_2\end{matrix}$, carbamide.

Amides may also be derived from the ammonium salts of organic acids by the subtraction of water:

$$HCOONH_4 - H_2O = HCO(NH_2).$$

3) Two hydrogens of the ammonia can be substituted by a di-valent rest, as, for instance:

a) $NH{=}CH_2$	b) $NH{=}CO$.
Methylene-imine (not known)	Carbimide

Compounds of this class are called *imides.* There are but few known which contain the NH group united to hydrocarbon

rests consisting only of hydrogen and carbon, but of the second class there are many representatives.

The group NH very frequently binds two carboxyl rests. Thus from the compound $\begin{matrix}CH_2{-}COOH\\ |\\ CH_2{-}COOH\end{matrix}$ (succinic acid), the body $\begin{matrix}CH_2{-}CO\\ |\\ CH_2{-}CO\end{matrix}\!\!>\!NH$ (succinimide), is derived. The imides may be considered as deduced from the amides by the subtraction of NH_3:

$$\underset{\text{Carbamide}}{CO\!<\!\begin{matrix}NH_2\\ NH_2\end{matrix}} = \underset{\text{Carbimide}}{CO{=}NH} + NH_3$$

$$\underset{\text{Succinamide}}{\begin{matrix}CH_2{-}CO{-}NH_2\\ |\\ CH_2{-}CO{-}NH_2\end{matrix}} = \underset{\text{Succinimide}}{\begin{matrix}CH_2{-}CO\\ |\\ CH_2{-}CO\end{matrix}\!\!>\!NH} + NH_3.$$

From the amic acids they are derived by the elimination of water:

$$\underset{\text{Carbamic acid}}{CO\!<\!\begin{matrix}NH_2\\ OH\end{matrix}} = \underset{\text{Carbimide}}{CO{=}NH} + H_2O$$

$$\underset{\text{Succinamic acid}}{\begin{matrix}CH_2{-}CO{-}NH_2\\ |\\ CH_2{-}CO{-}OH\end{matrix}} = \underset{\text{Succinimide}}{\begin{matrix}CH_2{-}CO\\ |\\ CH_2{-}CO\end{matrix}\!\!>\!NH} + H_2O.$$

4) All three hydrogen atoms of the ammonia can be replaced by one tri-valent hydrocarbon rest:

$$\underset{\substack{\text{Prussic acid}\\ \text{(Formonitrile)}}}{N{\equiv}CH} \qquad\qquad \underset{\substack{\text{Isocyanic acid}\\ \text{(Carbonitrile)}}}{N{\equiv}C(OH).}$$

Compounds of this class are called *nitriles.*

Besides the nitrogen derivatives of the carbon compounds in which the nitrogen is in *direct* union with the carbon, there are the esters of nitric and nitrous acids with alcohol rests. These have already been noticed. The nitrogen in them is bound to the carbon *through* oxygen. There is, however, a class of compounds derived from nitric acid, in which the nitrogen is bound directly to the carbon.

The hydroxyl of nitric acid can be replaced by a hydrocarbon rest in a manner analogous to the formation of sulphonic acids from sulphuric acid, $(HO)NO_2$, $CH_3{-}NO_2$.

Such compounds are called *nitro-compounds.* Their isomerism with the nitrous esters is evident from the following formulas:

$CH_3{}^-O{}^-NO$, CH_3NO_2, Nitrous-methyl ester, derived from HO.NO.

$CH_3{}^-NO_2$, CH_3NO_2, Nitromethane, derived from HO.NO_2.

It is a characteristic property of all nitro-compounds that they are converted into amido-compounds by the action of reducing agents (nascent hydrogen):

$$\underset{\text{Nitromethane}}{CH_3{}^-NO_2} + 3\,H_2 = \underset{\text{Methylamine}}{CH_3{}^-NH_2} + 2\,H_2O,$$

while the isomeric nitrous esters are reduced to ammonia and alcohol:

$$CH_3{}^-O{}^-NO + 3\,H_2 = CH_3OH + NH_3 + H_2O.$$

The nitro-compounds will be considered more at length under the aromatic series.

Amines.

a) *Primary amines,* those in which one H of the ammonia is substituted by a hydrocarbon rest.

b) *Secondary amines,* those in which two H's of the ammonia are substituted by hydrocarbon rests.

c) *Tertiary amines,* those in which all three of the H's of the ammonia are substituted by hydrocarbon rests.

The primary amine bases resemble ammonia in every respect. They possess nearly the same odor, are strong bases, and their chlorhydric acid salts give with platinic chloride double salts difficultly soluble in water, viz., $(CH_3NH_2 \,.\, HCl)_2PtCl_4$.

The secondary amine bases are very closely related to ammonia, and are also strong bases. They are less volatile than the primary amines, and their platinum chloride double salts are not so difficultly soluble.

The tertiary amine bases diverge still more in their chemical properties from ammonia. Their platinic chloride double salts are easily soluble, and their boiling points lie higher than those of the secondary amines. All three classes of amines, however, unite, like ammonia, directly with acids, viz., HCl, HBr, HI, HNO_3, H_2SO_4.

$NH_3 \cdot HCl$; $CH_3(NH_2) \cdot HBr$ (Methylammonium bromide); $(CH_3)_2NH \cdot HI$ (Dimethylammonium iodide);

$(CH_3)_3N \cdot HNO_3$ (Trimethylammonium nitrate); $CH_3(NH_2) \cdot H_2SO_4$ (Acid Methylammonium sulphate);

$[(CH_3)_2NH]_2 \cdot H_2SO_4$ (Neutral Dimethyl ammonium sulphate).

The amine is set free from these salts by an alkaline hydroxide:

$$CH_3(NH_2) \cdot HBr + KHO = CH_3NH_2 + KBr + H_2O$$
$$(CH_3)_2NH \cdot HI + KHO = (CH_3)_2NH + KI + H_2O$$
$$(CH_3)_3N \cdot HNO_3 + KHO = (CH_3)_3N + KNO_3 + H_2O.$$

If, however, the fourth replaceable hydrogen atom in an ammonium salt is substituted by a hydrocarbon rest, the substituted ammonium compound is obtained, viz., $(CH_3)_4NBr$, tetramethylammonium bromide. Alkalis do not set the bases free from these salts. By treatment with silver oxide, however, a base, $(CH_3)_4NOH$, tetramethylammonium hydroxide, is formed. This compound does not show the properties of ammonia, but resembles potassium hydroxide completely in its behavior. It possesses basic properties of a marked character, and forms salts by substitution.

We shall now pass to the individual description of the amines.

Methylamine, $CH_3{-}NH_2$, or CH_5N, is a gas which at a few degrees below zero condenses to a liquid. It has a strong ammoniacal odor, blues litmus paper, is very soluble in water, forms white clouds with chlorhydric acid gas, combines with acids to form crystallizable salts, and yields a difficultly soluble

platinum salt $(CH_5N \cdot HCl)_2PtCl_4$. It is inflammable and burns with a yellow flame.

Dimethylamine, $(CH_3)_2NH$, or C_2H_7N, is a colorless liquid with the odor of ammonia. It boils at 8°.

Trimethylamine, $(CH_3)_3N$, or C_3H_9N, is a liquid boiling at 9°. It forms salts with acids. In nature, it occurs in many plants, as the common pigweed, the flowers of the pear-tree, hawthorne, etc., and in the decomposition products of many animal and vegetable substances, viz., pickled herrings and yeast.

The salts of these amine bases are almost all soluble in water and alcohol.

The behavior of the nitrous salts of the amines is worthy of attention. It is well known that ammonium nitrite, by merely boiling its water solution, is decomposed into nitrogen and water :

$$NH_4{}^-NO_2 = N_2 + 2H_2O.$$

The nitrites of the primary amine bases behave in an analogous manner, their aqueous solutions being also decomposed on boiling. Instead of the formation of two molecules of water, however, one molecule of water and one molecule of alcohol are produced:

$$N(CH_3)H_3{}^-NO_2 = N_2 + CH_3OH + H_2O.$$

In order to produce such a decomposition, it is only necessary to boil the solution of a salt of the amine with a solution of potassium nitrite.

The secondary amine bases behave differently. If an aqueous solution of any of their salts is boiled with a potassium nitrite solution, a peculiar compound, the nitroso-derivative of the base is formed :

$$N(CH_3)_2H_2{}^-NO_2 = H_2O + \underset{\text{Methylnitroso-amine}}{N(CH_3)_2NO}.$$

The constitution of this compound is $N\begin{cases} CH_3 \\ CH_3 \\ N{=}O. \end{cases}$

The nitrites of the tertiary amines are decomposed with difficulty and yield finally the same nitroso-compounds as the secondary amines.

The nitroso-amines yield on reduction with zinc dust and acetic acid the *hydrazine compounds*, viz., $(CH_3)_2N{-}NO + 2\,H_2 = H_2O + (CH_3)_2N{-}NH_2$, dimethyl-hydrazine.

Tetramethylammonium iodide, $(CH_3)_4NI$, forms white crystals very difficultly soluble in alcohol. By digestion with moist silver oxide, the compound

Tetramethylammonium hydroxide, $(CH_3)_4N^-OH$, is obtained. White deliquescent crystals, with strongly basic properties, forming finely crystallizable salts.

Formation of the Amines.

The primary amines are formed :

1) By boiling the cyanic ethers with an alkali hydroxide :

$$\underset{\text{Methyl cyanic ether}}{CON^-CH_3} + 2\,KHO = K_2CO_3 + \underset{\text{Methylamine}}{CH_3^-NH_2}.$$

2) By reducing the nitro-compounds with nascent hydrogen :

$$CH_3^-NO_2 + 6\,H = CH_3^-NH_2 + 2\,H_2O.$$

3) By reducing the cyan-compounds with nascent hydrogen :

$$\underset{\text{Cyanhydric acid}}{HCN} + 4\,H = H_3C^-NH_2.$$

4) (In the form of the halogen salts.) By the action of alcoholic ammonia on the chlorides, bromides, and iodides of the hydrocarbons :

$$CH_3I + NH_3 = CH_3(NH_2)HI.$$

The secondary amines are formed by the action of the iodides (chlorides or bromides) of the hydrocarbons on the primary amines :

$$CH_3I + CH_3^-NH_2 = (CH_3)_2NH\,.\,HI.$$

The tertiary amines are formed by the action of the iodides, etc., on the secondary amines :

$$CH_3I + (CH_3)_2NH = (CH_3)_3N + HI.$$

The substituted ammonium bases are formed by the further action of the iodides, etc., on the tertiary amines :

$$CH_3I + (CH_3)_3N = (CH_3)_4NI.$$

It is hence possible to build up in this manner the completely substituted amines from the primary amines.

By the action of ammonia on the iodides, etc., of the hydrocarbons, not only the primary amines are formed, but also both the others, as well as the substituted ammoniums. The reason of this is that all the different reactions take place at the same time.

Amides and Amic Acids.

When the hydroxyl group of a monobasic acid is replaced by the amido-group NH_2, an *amide* is formed. Formic acid, HCOOH, gives formamide, $HCO(NH_2)$. It is produced by heating formic ester with gaseous ammonia:

$$\underset{\text{Ethyl formic ester}}{CHOOC_2H_5} + NH_3 = \underset{\text{Formamide}}{CHO(NH_2)} + \underset{\text{Alcohol}}{C_2H_5OH}.$$

Colorless liquid, easily soluble in water. Boils at 194°. Acids and bases convert it into formic acid and ammonia:

$$CHO(NH_2) + H_2O = CHOOH + NH_3.$$

On distillation with anhydrous phosphoric acid, water is split off and the nitrile is produced:

$$CHO(NH_2) = CHN + H_2O.$$

The hypothetical carbonic acid is dibasic, $CO\langle^{OH}_{OH}$, and yields an amic acid and amide.

Carbamic acid, carbaminic acid, $CO\langle^{NH_2}_{OH}$. The acid is not known in the free state. Its salts and esters, however, exist. The ammonia salt is formed on the contact of dry carbonic acid and ammonia gas:

$$CO_2 + 2\,NH_3 = CO(ONH_4)(NH_2).$$

Water decomposes the salt into ammonium carbonate:

$$CO(ONH_4)(NH_2) + H_2O = (NH_4)_2CO_3.$$

The esters of carbamic acid are called *urethanes,* as, for example, methyl urethane, $CO\langle^{NH_2}_{OCH_3}$, which is formed by leading chlorcyan into methyl alcohol.

Carbamide, Urea, $CO\langle^{NH_2}_{NH_2} = CH_4N_2O$.

Urea occurs in the urine of all mammiferous animals, particularly in that of the carnivora. It is found also in the blood, liver, bile, lymph, and, in certain pathological conditions, in all the animal fluids. It is formed by the action of phosgen gas on ammonia:

$$COCl_2 + 2\,NH_3 = CO(NH_2)_2 + 2\,HCl.$$

And by heating ammonium cyanate:

$$CON(NH_4) = CO(NH_2)_2.$$

In the latter case there is a shifting of the atoms, which is termed *atomic migration.* It is also formed from uric acid, creatinine, and urethane.

It is usually made either from human urine or from ammonium cyanate. From the former it is obtained by evaporating to a thin syrup, and acidifying with nitric acid. The urea separates in the form of the difficultly soluble urea nitrate. From ammonium cyanate it is produced in the following manner: Potassium cyanate is boiled with ammonium sulphate, whereby potassium sulphate and ammonium cyanate are formed. The latter is then transposed into urea.

Urea crystallizes in four-sided, rhombic, striated prisms, which fuse at 120° and decompose at a higher temperature. It is odorless, and has a bitter, cooling taste like saltpetre. Water dissolves about its own weight of it at the ordinary temperature, suffering a considerable reduction of temperature. At 100° it is soluble in all proportions in water. In alcohol it is easily soluble, in ether, almost insoluble.

Its solution is neutral to test-paper. It combines with both bases and acids to form salts.

With HCl: CON_2H_4, HCl, hydrochloride.
With HNO_3: CON_2H_4, HNO_3, nitrate. Difficultly soluble in water and nitric acid, and hence well adapted for the separation of urea from its solutions.
With HgO: CON_2H_4, HgO.

With sodium salts, as for instance, with NaCl :

$$CON_2H_4 + NaCl + H_2O.$$

It unites further with many other salts, among which the compounds with mercuric nitrate and chloride deserve special mention.

Decompositions of Urea. 1) Urea when heated to 150°–170° evolves ammonia and passes into *biuret*,

$$C_2H_5N_3O_2 :$$

$$2\,CH_4N_2O_2 = C_2H_5N_3O_2 + NH_3.$$

Biuret, $CO\langle^{NH_2}_{NH}\rangle CO\langle^{NH_2}$, forms colorless needles difficultly soluble in water.

2) By the action of chlorine, urea yields cyanuric acid (vide supra), ammonium chloride, chlorhydric acid, and nitrogen.

If water is present, however, chlorine oxidizes it to carbonic acid, chlorhydric acid, and nitrogen :

$$3\,CH_4N_2O + 6\,Cl = \underset{\text{Cyanuric acid}}{C_3H_3N_3O_3} + NH_4Cl + 5\,HCl + N_2.$$

3) Urea falls into ammonia and cyanic acid on heating with a solution of silver nitrate, or with phosphoric anhydride, or by itself :

$$CON_2H_4 = CONH + NH_3.$$

4) Urea is converted into ammonium carbonate by heating with water at a high pressure, or by boiling with acids or alkalis :

$$CON_2H_4 + 2\,H_2O = (NH_4)_2CO_3.$$

Urea suffers the same change rapidly and at ordinary temperature when putrefying substances, such as urine, are present.

5) By the action of nitrous anhydride, urea is resolved into carbonic acid and nitrogen :

$$CON_2H_4 + N_2O_3 = CO_2 + 2\,H_2O + 2\,N_2.$$

Urea can be estimated quantitatively by means of mercuric nitrate, which forms with urea a white, insoluble precipitate :

$$CH_4N_2O + 2\,HgO + HNO_3.$$

The hydrogen atoms in urea can be replaced by mono-valent atomic groups. The greater number of the known compounds of this class, however, are substitutions of one or two atoms of hydrogen. The following are known :

$CO\langle^{NH(CH_3)}_{NH_2}$ Methylurea,
$CO\langle^{NH(CH_3)}_{NH(CH_3)}$ Dimethylurea,
$CO\langle^{NH(C_2H_5)}_{NH_2}$ Ethylurea,
$CO\langle^{NH(C_2H_5)}_{NH(C_2H_5)}$ Diëthylurea,
$CO\langle^{N(C_2H_5)_2}_{NH(C_2H_5)}$ Triethylurea,
$CO\langle^{N(C_2H_5)_2}_{N(C_2H_5)_2}$ Teträethylurea,
$CO\langle^{NH(C_2H_3O)}_{NH_2}$ Acetylurea, etc.

Substituted ureas may be produced :

1) By heating urea with amine bases, aci-chlorides, and acid anhydrides :

2) By boiling potassium cyanate with the sulphates of the amine bases :

3) By the action of carbon oxy-chloride on the amine bases.

The following compounds are also derived from urea :

Allophanic acid, $CO\langle^{NH\text{-}COOH}_{NH_2} = C_2H_4N_2O_3$,

Biuret, . . . $CO\langle^{NH\text{-}CO\text{-}NH_2}_{NH_2} = C_2H_5N_3O_3$ (v. s.).

The esters of allophanic acid are formed when cyanic acid gas is led into an alcohol :

$$2\,CONH + CH_4O = C_3H_6N_2O_3 = CO\langle^{NH_2}_{NH\text{-}COOCH_3}.$$

Sulphocarbamic acid, sulphocarbaminic acid, corresponding to carbamic acid, $CO(SH)(NH_2)$. The free acid is very

unstable. Its ammonium salt is obtained by the action of carbon disulphide on alcoholic ammonia.

Sulphocarbamide, thiurea, $CS\langle^{NH_2}_{NH_2}$, corresponding to urea, $CO\langle^{NH_2}_{NH_2}$, is obtained from ammonium sulphocyanate.

Its formation is entirely analogous to that of urea from ammonium cyanate:

$$\underset{\text{Am. cyan.}}{CON(NH_4)} = \underset{\text{Urea}}{CO(NH_2)_2}$$

$$\underset{\text{Am. sulphocyan.}}{CSN(NH_4)} = \underset{\text{Sulpho-urea}}{CS(NH_2)_2}.$$

Dry ammonium sulphocyanate is heated for some time at 140°. Only a part of it, however, is converted into thiurea. Sulphocarbamide crystallizes in long, colorless needles or prisms, fusing at 140°. It combines with acids like urea.

The representative of the following group can be derived from urea by the replacement of the oxygen by the di-valent ammonia rest, the imido-group, just as thiurea is derived from urea by the replacement of the oxygen by sulphur.

$$CO\langle^{NH_2}_{NH_2} \qquad\qquad \underset{\text{Imido-urea}}{C(NH)\langle^{NH_2}_{NH_2}}.$$

Guanidine, *Imido-urea,* $C(NH)\langle^{NH_2}_{NH_2} = CN_3H_5$. Guanidine is produced by the decomposition of guanine. It is formed from cyanamide and ammonium chloride:

$$\underset{\text{Cyanamide}}{CN(NH_2)} + NH_4Cl = C(NH)\langle^{NH_2}_{NH_2} \,.\, HCl.$$

This manner of formation depends on an atomic migration similar to that occurring in the synthesis of urea:

$$\underset{\text{Cyanic acid}}{CONH} + NH_3 \quad \text{gives} \quad \underset{\text{Urea}}{CO(NH_2)_2}$$

$$\underset{\text{Cyanamide}}{CN(NH_2)} + NH_3 \quad \text{gives} \quad \underset{\text{Guanidine}}{C(NH)(NH_2)_2}.$$

It can also be produced by the action of iodocyan on ammonia, the reaction proceeding on two steps:

$$\underset{\text{Iodocyan}}{CNI} + NH_3 = \underset{\text{Cyanamide}}{CNNH_2} + HI,$$

$$\underset{\text{Cyanamide}}{CNNH_2} + NH_3 = C(NH)(NH_2)_2.$$

The ammonium sulphocyanate first changes into thiurea, then splits off H_2S and passes into cyanamide, which, with the ammonium sulphocyanate, is transposed into guanidine sulphocyanate:

1) $\underset{\substack{\text{Ammonium}\\\text{sulphocyanate}}}{CSN{-}NH_4} = \underset{\text{Thiurea}}{CS(NH_2)_2}.$

2) $CS(NH_2)_2 = H_2S + \underset{\text{Cyanamide}}{CN(NH_2)}.$

3) $CN(NH_2) + NH_3 \,.\, HSCN = \underset{\text{Guanidine sulphocyanate}}{C(NH)(NH_2)_2 \,.\, HSCN}.$

Guanidine is a colorless, easily soluble, and crystalline body, with strong basic properties. It takes up carbonic acid from the air. The nitrate $CH_5N_3 \,.\, HNO_3$ is difficultly soluble.

The Nitrile of Methane.

The nitrile and its derivatives, among which are the imido-compounds, form a large, important, and well defined group. The fundamental compound has the composition HCN, and as the H can be substituted by many other atoms and atomic groups, it is convenient to consider it as a compound of the mono-valent group CN with H. The group CN is called the cyan-group, and is often written Cy.

Cyanhydric Acid, Hydrocyanic Acid, *Prussic acid.* HCN, or HCy. Cyanhydric acid does not occur in the free state in nature. It is a decomposition product of certain highly constituted compounds which occur in the kernels of peach and cherry-pits, and the flowers of the amygdaleæ, etc.

The potassium compound, KCN, is formed from its three elements when they are subjected to a very high temperature. By passing ammonia over glowing carbon, the ammonium salt is obtained. Cyanhydric acid can, hence, be produced from

inorganic substances. The ammonium compound is also formed by heating ammonium formate :

$$2\,CHO_2(NH_4) = CN(NH)_4 + CO + 3\,H_2O.$$

Sodium cyanide is formed when nitrogenous substances are heated with sodium (qualitative test for nitrogen).

Ammonium cyanide is also formed by passing a mixture of the vapors of chloroform and ammonia gas through a tube heated to 300° :

$$CHCl_3 + 5\,NH_3 = \underset{\text{Ammonium cyanide}}{CN(NH_4)} + 3\,NH_4Cl.$$

If potassium hydroxide is added to a solution of a chloroform and alcohol in ammonia, a violent reaction takes place at ordinary temperatures, and potassium cyanide is formed :

$$CHCl_3 + NH_3 + 4\,KHO = \underset{\text{Potassium cyanide}}{CNK} + 3\,KCl + 4\,H_2O.$$

Cyanhydric acid is manufactured from potassium ferrocyanide, a complicated cyanogen compound, $K_4Fe(CN)_6$, and dilute sulphuric acid. 10 parts of the ferrocyanide are mixed with 7 parts of sulphuric acid and 15–20 parts of water, and the whole distilled. A dilute cyanhydric acid is obtained, which is freed from water by means of calcium chloride.

Cyanhydric acid is a colorless liquid, boiling at 27° and solidifying at −15°. It is miscible with water, alcohol, and ether, and burns with a blue flame. It is extremely poisonous. In a dilute state its odor, which resembles that of bitter almonds, causes giddiness and a disagreeable roughness in the throat. On standing it soon decomposes. Its solution in water is more stable, particularly when a drop of sulphuric acid, or a small piece of phosphorus is added to it. Chlor- brom- and iodohydric acid gases combine with it, forming solid white compounds.

Although cyanhydric acid scarcely reddens litmus paper, it is a well-defined acid, its hydrogen being easily replaced by metals. Its most important salts are :

Potassium Cyanide, KCN, or KCy. This salt is produced by fusing anhydrous potassium ferrocyanide under exclusion of air, with or without the addition of potassium carbonate.

The potassium cyanide thus obtained is not pure, as it contains potassium cyanate and carbonate, but it can be used for most purposes. Pure potassium cyanide can be made by passing cyanhydric acid into an alcoholic solution of potassium hydroxide. The potassium cyanide, which is insoluble in alcohol, is precipitated.

Potassium cyanide crystallizes in cubes, is easily soluble in water, deliquescent when exposed to the air, and almost insoluble in absolute alcohol. Its aqueous solution decomposes rapidly, potassium and ammonium formates and a brown amorphous mass being produced:

$$KCN + 2\,H_2O = CHKO_2 + NH_3.$$

Potassium cyanide always has the odor of cyanhydric acid, because the carbonic acid contained in the air sets the acid free. In a dry state it is very stable. When heated, so long as it is not exposed to the oxygen of the air, or when the air is excluded, it can be fused and even volatilized; by heating in the presence of air, however, it is decomposed into potassium cyanate:

$$CNK + O = CNOK.$$

Metallic oxides act in the same manner, but more energetically. Fused with sulphur, or sulphides, it yields potassium sulphocyanate:

$$CNK + S = CNSK.$$

Owing to its power of taking up oxygen, it is a powerful reducing agent. It is largely used in the arts (electroplating, etc.).

Ammonium cyanide, $(NH)_4CN$, is formed by the action of ammonium chloride on potassium cyanide. It sublimes at 36° and is extremely poisonous.

Silver cyanide, AgCN, is obtained by the precipitation of potassium cyanide with silver nitrate. It is insoluble in water and nitric acid,

soluble in an excess of potassium cyanide, forming a crystalline double salt, CNAgCNK, soluble in water. The double cyanides of silver, gold, and nickel are employed in electro-plating.

Mercury cyanide, $Hg(CN)_2$, is obtained by dissolving mercuric oxide in aqueous cyanhydric acid. Finely crystallizable salt, soluble in water.

If a solution of potassium cyanide is boiled with a solution of a ferrous salt, *e. g.*, with ferrous sulphate, a peculiar compound of ferrous cyanide and potassium cyanide is formed, $Fe(CN)_2 + 4\,KCN$. This body is not a double salt of the two cyanides, and reagents do not decompose it into the respective cyanides. The six cyan-groups are intimately united with each other and with the iron, forming an atomic complex which possesses four free attractive energies, satisfied in the above case by four potassium atoms. The potassium in this compound can easily be replaced by other metals, or it can be replaced by hydrogen atoms, giving rise to a compound which in all its properties is a well-characterized acid.

The tetra-valent group, $Fe(CN)_4$, is termed *ferrocyan*, or *prussan*, and for the sake of brevity is often written Cfy.

Potassium Ferrocyanide, *Yellow Prussiate of Potash*, $K_4Fe(CN)_6$, forms the starting-out point for the production of all cyanogen compounds. Its formation from potassium cyanide has already been given.

It is prepared on a large scale by melting together in large iron pots crude potassium carbonate (potash), animal waste (horn, leather, blood, etc.), and iron scrap, then cooling, lixiviating, and crystallizing. By the fusion of the above substances, potassium cyanide is produced from the carbon and nitrogen existing in the animal matters. The potassium sulphate which exists in the potash is reduced by the iron, forming ferrous sulphide. On lixiviation these two compounds react on each other, yielding potassium ferrocyanide and sulphide:

$$FeS + 6\,KCN = K_4Fe(CN)_6 + K_2S.$$

Potassium ferrocyanide crystallizes in yellow quadratic prisms with three molecules of water: $K_4Fe(CN)_6 + 3\,H_2O$. It is stable in the air, soluble in four parts of water, and insol-

uble in alcohol. It is not poisonous. At 100° it loses its water slowly, becoming white, but on exposure to the air it gradually regains its water of crystallization and its color. At a temperature near the red heat it fuses and decomposes into potassium cyanide, carbon, iron, and nitrogen :

$$K_4Fe(CN)_6 = 4\,KCN + 2\,C + Fe + N_2.$$

By heating with concentrated sulphuric acid, carbonous oxide is evolved :

$$K_4Fe(CN)_6 + 6\,H_2SO_4 + 6\,H_2O = 2\,K_2SO_4 + FeSO_4 + 3\,(NH_4)_2SO_4 + 6\,CO.$$

Heated with dilute sulphuric, however, cyanhydric acid is set free, and *potassium ferrous ferrocyanide*, an insoluble compound, is formed :

$$2\,K_4Fe(CN)_6 + 3\,H_2SO_4 = 3\,K_2SO_4 + K_2Fe_2(CN)_6 + 6\,CNH.$$

In the former case the cyanhydric acid as it is formed breaks into carbonous oxide and ammonia :

$$CHN + H_2O = CO + NH_3.$$

Oxidizing agents, such as an aqueous solution of chlorine, abstract from two molecules of potassium ferrocyanide two molecules of potassium, forming *potassium ferricyanide*, or *red prussiate of potash.*

$$2\,K_4Fe(CN)_6 + Cl_2 = 2\,KCl + K_6Fe_2(CN)_{12}.$$

Nitric acid converts the yellow prussiate into *potassium nitroprusside:*

$$K_4Fe(CN)_6 + 3\,HNO_3 = K_2Fe(CN)_5(NO) + 2\,KNO_3 + CO_2 + NH_3.$$

By the action of dilute acids, the potassium in potassium ferrocyanide is replaced by hydrogen, forming

Hydroferrocyanic acid, $H_4Fe(CN)_6$. This body is a strong acid in which the four basic hydrogen atoms can be replaced by the same or different metals. On exposure to the air it rapidly turns blue, owing to the formation of Prussian blue.

Ferric Ferrocyanide, $(Fe_2)_2[Fe(CN)_6]_3$, **Prussian Blue.** This salt is formed by the action of a soluble ferrocyanide on a soluble ferric salt, as ferric chloride :

$$3\,K_4FeCy_6 + 2\,Fe_2Cl_6 = (Fe_2)_2[Fe(CN)_6]_3 + 12\,KCl.$$

It is a dark-blue compound, insoluble in water and dilute acids, but soluble in an excess of potassium cyanide, or oxalic acid solutions. Its formation is a characteristic test for the presence of a ferrocyanide, and since all cyan compounds can be converted into potassium ferrocyanide (by boiling with potassium hydroxide and ferrous sulphate), it serves as a general test for their presence.

Ferrous salts give with soluble ferrocyanides a white precipitate, which, when exposed to the air, turns blue, owing to oxidation.

Copper salts give a characteristic reddish brown precipitate of *cupric ferrocyanide.*

Potassium Ferricyanide, *Red Prussiate of Potash*, $K_6Fe_2(CN)_{12}$, is obtained by leading chlorine into a solution of potassium ferrocyanide. It forms deep red crystals, easily soluble in water but insoluble in alcohol. With ferric salts, it yields a deep blue precipitate, called *Turnbull's blue*, which resembles Prussian blue very much. Solutions of ferric salts are colored brown, but not precipitated by it.

Hydroferricyanic acid, $H_6Fe_2(CN)_{12}$, is formed by the action of acids on potassium ferricyanide. Brownish deliquescent needles, quickly turning blue on exposure to the air.

Nitroprusside compounds, as already stated, are formed from the ferrocyanides by the action of nitric acid. The sodium salt, $NaFeCy_5(NO)$, is the most important. It crystallizes in beautiful, ruby, rhombic needles. Soluble nitroprussides are a most extremely delicate test for soluble sulphides, giving a purple-red color with them, which, however, soon fades out.

Corresponding to the ferrocyanides there are series of compounds in which the iron is replaced by manganese, chromium, and cobalt.

Potassium manganocyanide, $K_4MnCy_6 + 3\,H_2O$, deep-blue quadratic tablets. *Potassium manganicyanide*, $K_6Mn_2Cy_{12}$, deep-red rhombic prisms.

Both of these compounds are easily decomposable. *Potassium chromicyanide*, $K_6Cr_2Cy_{12}$, bright-yellow prisms, also easily decomposable. The most stable of this series are the cobalticyanides, of which *potassium cobalticyanide*, $K_6Co_2(CN)_{12}$, crystallizing in yellow prisms, and *hydrocobalticyanic acid*, $H_6Co_2(CN)_{12}$, forming white-fibrous crystals, are the most prominent.

The H in cyanhydric acid can be substituted, not only by metals, but also by the halogens—chlorine, bromine, and iodine.

Chlorcyan, cyanogen chloride, CNCl. There are two modifications of this body, one a solid and the other a liquid. The difference between them lies in their molecular weight, the liquid one having the formula CNCl, while the solid is three times as large, $C_3N_3Cl_3$.

Chlorcyan, CNCl, is obtained by acting on mercuric cyanide with chlorine at $-7°$. It is a colorless liquid, boiling at 15°. When pure, it will keep for a long time unchanged, but when impure it soon passes into the solid chlorcyan.

Tri-chlorcyan, $C_3N_3Cl_3$, is formed from the preceding compound; or it can be made by passing chlorine into anhydrous cyanhydric acid exposed to direct sunlight. It crystallizes in needles or leaflets, which fuse at 145° and boil at 190°. It is very poisonous.

Mercuric cyanide treated with bromine yields *bromcyan*, CNBr. Long needles, boiling at 150°.

With iodine, mercury cyanide forms *iodocyan*, CNI. Fine-white needles, which sublime at 45°, possess a penetrating odor, and are poisonous.

The chlorine, bromine, and iodine in the cyan compounds can easily be replaced by mono-valent atomic groups:

$$2\,KHO + CNCl = KCl + \underset{\text{Potassium cyanate}}{CN(OK)} + H_2O$$

$$2\,NH_3 + CNCl = NH_4Cl + \underset{\text{Cyanamide}}{CN(NH_2)}, \text{ etc.}$$

The H in cynahydric acid can also be replaced by alcohol rests, thus giving rise to organic cyanides. A difference in the binding of the atoms of cyanhydric acid, which has as yet not appeared in the compounds so far considered, must now be mentioned.

It is a well-known fact in inorganic chemistry that nitrogen acts both as a tri-valent and penta-valent element. Cyanhydric acid may be considered, therefore, not only as a compound in which a tetra-valent carbon atom holds together a tri-valent nitrogen atom and a mono-valent hydrogen atom, $H^-C{\equiv}N$, but as one in which a penta-valent nitrogen atom binds a tetra-valent carbon atom and a mono-valent hydrogen atom, $H^-N{\equiv}C$. In the former case, the hydrogen is bound to the carbon, forming a CH-group, which is united to the nitrogen; while in the latter, the H is bound to N, forming an NH-group, which is united to carbon. Cyanides most probably consist of a mixture of both of these modifications, which, on account of the great similarity of their reactions, have not as yet been separated. In the compounds of cyan with hydrocarbon rests, however, the isomerism is very marked.

Cyanmethyl, Methyl Cyanide, $H_3C^-C{\equiv}N = C_2H_3N$. The CH_3 is bound to the C of the cyan. It is formed by the distillation of potassium methylsulphate with potassium cyanide; or by digestion of methyl iodide with potassium cyanide: $CH_3I + KCN = CH_3CN + KI$.

It is a liquid boiling at 82°, with an ethereal odor, and miscible with water. On boiling with acids or alkalis, it falls into acetic acid and ammonia:

$$H_3C^-CN + KHO + H_2O = \underset{\text{Potassium acetate}}{H_3C^-CO_2K} + NH_3.$$

It is also produced by the action of dehydrating agents on acetamide. Phosphoric anhydride, for instance, extracts a molecule of water from acetamide:

$$\underset{\text{Acetamide}}{C_2H_3ONH_2} - H_2O = \underset{\text{Methyl cyanide}}{C_2H_3N}.$$

It is hence also called *aceto-nitrile.* Sodium converts it into the polymeric *methyl cyanurate,* or *kyanmethyl,* $(CH_3^-CN)_3$, a basic compound fusing at 180°.

Methylcarbammonium, Methyl Isocyanide, H_3C^-NC (the CH_3 is bound to the N of the cyan). It is formed by the

action of one molecule of methyl iodide on two molecules of silver cyanide. A double compound of methyl cyanide and silver cyanide is first formed, which is decomposed by the potassium cyanide. By the distillation of potassium methyl-sulphate with potassium cyanide, it is produced together with the normal methyl cyanide. It is also obtained by digesting chloroform with methylamine in the presence of potassium hydroxide:

$$CH_3NH_2 + CHCl_3 = CH_3NC + 3\,HCl.$$

This is the same reaction as the one by which cyanhydric acid is formed from chloroform and ammonia (p. 54). If instead of ammonia the methylated ammonia (methylamine) is taken, a methylated cyanhydric acid (methyl isocyanide) is produced instead of cyanhydric acid.

Methyl isocyanide is a liquid boiling at 59°. It has a most disagreeable odor, and is not miscible with water. It is hardly acted on by alkalis, but acids decompose it easily into methylamine and formic acid :

$$H_3C^-NC + HCl + 2\,H_2O = H_3CNH_2\,.\,HCl + CH_2O_2.$$

It is well known that cyanhydric acid, by taking up two molecules of water, falls into formic acid and ammonia :

$$HCN + 2\,H_2O = HCOOH + NH_3.$$

Both the methyl cyanides, or methylated cyanhydric acids, suffer the same decomposition, the one by the action of alkalis, the other by acids. In the case of methyl cyanide the products of the decomposition are methylated formic acid (acetic acid) and ammonia, while from the methyl isocyanide, formic acid and methylated ammonia (methylamine) are formed :

$$\underset{\text{Methyl cyanide}}{H_3C^-CN} + 2\,H_2O = \underset{\text{Acetic acid}}{H_3C^-COOH} + NH_3.$$

$$\underset{\text{Methyl isocyanide}}{H_3C^-NC} + 2\,H_2O = \underset{\text{Methylamine}}{H_3C^-NH_2} + \underset{\text{Formic acid}}{CHOOH}.$$

The cause of this difference in the reactions is that in methyl cyanide the methyl is bound to the carbon, while in the methyl isocyanide it is bound to the nitrogen of the cyan. The binding is not broken in the reaction.

All cyanides are decomposed by boiling with acids or alkalis. Normal cyanides yield acids of higher carbon content and ammonia. Isocyanides give formic acid and amine bases.

Compounds of Cyanic Acid.

There are two series of cyanic acid compounds. The first is derived from carbimide, CONH, the second from cyanhydroxyl, CNOH. In the first series the O is bound to the C by both its bonds, and the N by two. The third bond of the N is satisfied by an H. In the second series the N is bound to the C by its three bonds, and O by one bond. The second bond of the O is satisfied by an H. The first series comprises the normal cyanic acid compounds, the second, the isocyanic acid compounds.

Cyanic Acid, CONH, is a gas with a piercing odor. Under 0° it condenses to a liquid. With water it soon breaks into carbonic acid and ammonia :

$$CONH + H_2O = CO_2 + NH_3.$$

It changes easily into a polymeric solid porcelain-like mass called *cyamelid.* Cyanic acid is formed by heating cyanuric acid.

Cyanuric Acid, $C_3O_3N_3H_3$, has a molecular weight three times as great as cyanic acid. It is obtained by the action of water on solid chlorcyan :

$$C_3N_3Cl_3 + 3\,H_2O = C_3O_3N_3H_3 + 3\,HCl.$$

And also by heating urea saturated with chlorhydric acid to 150°:

$$3\,CO(NH_2)_2 = C_3O_3N_3H_3 + 3\,NH_3.$$

The acid crystallizes with two molecules of water.

Cyanic acid is monobasic. Cyanuric acid is tribasic, and forms three series of salts.

Potassium Cyanate, CONK, is obtained by fusing potassium cyanide with minium, Pb_3O_4. It crystallizes in thick short needles or leaflets, and is easily decomposed into potassium carbonate and ammonia :

$$CONK + 2\,H_2O = KHCO_3 + NH_3.$$

Potassium Isocyante, CNOK, is formed by the action of potassium hydroxide on iodocyan :

$$CNI + 2\,KHO = CNOK + KI + H_2O.$$

It crystallizes in finely felted needles.

Ammonium Cyanate, $CON(NH_4)$, is produced by mixing cyanic acid gas and ammonia gas. By boiling with water it is transformed into urea :

$$CON(NH_4) = CO\langle\begin{matrix}NH_2\\NH_2\end{matrix}.$$

Methyl cyanic ether, $CON(CH_3)$, is formed, together with methyl cyanuric ether, by the distillation of potassium methylsulphate with potassium cyanate. It is a very volatile liquid, possessing a powerful odor which causes weeping. By the action of ammonia, methylurea is produced :

$$CON(CH_3) + NH_3 = CO\langle\begin{matrix}NH(CH_3)\\NH_2\end{matrix}.$$

It is converted by boiling with potassium hydroxide solution into methylamine and potassium carbonate :

$$CON(CH_3) + 2\,KHO = K_2CO_3 + CH_3(NH_2).$$

Methyl isocyanic ether, $CNO(CH_3)$, is produced by the action of sodium methoxide on chlorcyan :

$$CNCl + CH_3ONa = CNOCH_3 + NaCl.$$

Methyl cyanuric ether, $C_3O_3N_3(CH_3)_3$, is polymeric with methyl cyanic ether. It is a white crystalline compound, fusing at 175° and boiling at 295°. On boiling with potassium hydroxide it also yields methylamine.

Corresponding to the two series of cyanic acid compounds there are two series in which the oxygen is replaced by sul-

phur, viz., the sulphocyanic acid and isosulphocyanic acid compounds.

Sulphocyanic Acid, CN^-SH, is an oily liquid with an odor resembling acetic acid. It breaks very easily into cyanhydric acid and persulphocyanic acid. $C_2N_2H_2S_3$.

Potassium Sulphocyanate, CN^-SK, is obtained by fusing potassium cyanide with sulphur. It crystallizes in prisms resembing nitre, is deliquescent, and very easily soluble in water with considerable reduction of temperature. Soluble ferric salts give a red color with it even in very dilute solutions.

Ammonium Sulphocyanate, NH_4SCN, is formed on bringing together carbon disulphide and ammonia:

$$CS_2 + 2\,NH_3 = CSN(NH_4) + H_2S.$$

Colorless, deliquescent tablets, easily soluble in water and alcohol. At 140° it is partially decomposed into thiurea:

$$CSN(NH)_4 = CS\langle\begin{matrix}NH_2\\NH_2\end{matrix}.$$

At 180°, however, it passes into guanidine sulphocyanate (p. 53).

The ethers of the sulphocyanic acids bear different names. Those of the normal sulphocyanic acid, CN^-SH, are called sulphocyanic ethers, but those of the isosulphocyanic acid are known as *mustard oils,* or *thio-carb-alkylamines.*

Methyl sulphocyanic ether, $CN(SCH_3)$, is made by the action of potassium methylsulphate, or methyl iodide, on potassium sulphocyanate. It is a colorless liquid, boiling at 133°, with the odor of leeks. Nascent hydrogen converts it into methylamine and methyl mercaptan:

$$CNSCH_3 + 2\,H_2 = CH_2S + CH_3NH_2.$$

On heating to 130° it passes partly into the polymeric compound, methyl sulphocyanuric ether, a crystalline body fusing at 188°, and partly into the isomeric methyl mustard oil.

Methyl mustard oil, methyl thiocarbamine, $CS(NCH_3)$, is formed

from the methylamine salt of methylsulphocarbamic acid (obtained by bringing together carbon disulphide and methylamine), $CS\begin{matrix}SH(CH_5N)\\NH(CH_3)\end{matrix}$, and mercuric chloride:

$$CS\begin{matrix}SH(CH_5N)\\NH(CH_3)\end{matrix} + HgCl_2 = CSN(CH_3) + HgS + CH_5N \,.\, HCl + HCl.$$

It is a white, crystalline compound, fusing at 34° and boiling at 119°. It has the piercing odor of horse-radish. Nascent hydrogen converts it into methyl-sulphaldehyde and methylamine:

$$CSNCH_3 + 2\,H_2 = CH_2S + CH_5NH_2.$$

If the H of cyanhydric acid is replaced by a cyan group, we obtain:

Cyan, or *Cyanogen,* $CN^{-}CN$, or C_2N_2. It is produced by heating mercuric or argentic cyanide, or by heating ammonium oxalate, or oxamide, with a dehydrating agent, as phosphoric anhydride:

$$\underset{\substack{\text{Ammonium}\\\text{oxalate}}}{C_2O_4(NH_4)_2} - 4\,H_2O = \underset{\text{Cyan}}{C_2N_2},$$

$$\underset{\text{Oxamide}}{C_2O_2(NH_2)_2} - 2\,H_2O = C_2N_2.$$

It exists in the gases of the blast furnace.

Inversely, the aqueous solution of cyan takes up water and passes gradually into ammonium oxalate:

$$C_2N_2 + 4\,H_2O = C_2O_4(NH_4)_2.$$

Cyan is a colorless gas with a suffocating odor. It condenses to a liquid at −25°, is combustible and burns with a red flame.

Its aqueous solution decomposes rapidly with the separation of a brown amorphous mass known as *azulmic acid,* $C_4N_4H_4O_2$; ammonium carbonate, cyanate, and oxalate are also formed.

Mercuric cyanide when heated leaves a brown amorphous residue, the composition of which is the same as that of cyan,

but its molecular weight is not known. It is called *paracyan*, or *para cyanogen*. On being heated to a red heat it passes into cyan.

By treating chlorcyan with ammonia we obtain

Cyanamide, $CN^{-}NH_2$, or $C\begin{matrix}\diagup NH \\ \diagdown NH\end{matrix}$, CN_2H_2.

$$CNCl + 2\ NH_3 = CN(NH_2) + NH_4Cl.$$

Crystalline compound fusing at 40°, soluble in water, alcohol, and ether. In ammoniacal aqueous solution it changes gradually into *dicyandiamide, or param*, $(CN)_2(NH_2)_2$, which crystallizes in rhombic tablets fusing at 205°, and is converted by acids into the basic *dicyandiamidine*, $C_2N_4H_6O$. Heated to 150° cyanamide passes into the trimolecular *cyanuramide*, $C_3N_3(NH_2)_3$, or *melamine*, which crystallizes in octahedrons.

Between melamine, $(CN)_3(NH_2)_3$, and cyanuric acid, $(CN)_3(OH)_3$, stands *ammeline*, $(CN)_3(NH_2)_2OH$, which is obtained by the action of potassium hydroxide on melamine :

$$(CN)_3(NH_2)_3 + KOH = (CN)_3(NH_2)_2OK + NH_3.$$
Potassium ammelide

Among the nitro-compounds of methane we shall consider the following :

Nitromethane, $CH_3^{-}NO_2$, is formed by the action of silver nitrite on methyl iodide. It is a liquid boiling at 101°. With nascent hydrogen it yields methylamine ; with sodium hydroxide, *sodium nitromethane* is formed, CH_2NaNO_2. The latter is a white solid substance which gives with bromine *bromnitromethane*, CH_2BrNO_2, and with nitrous acid *methylnitrolic acid*, $CH(NO_2)N^{-}OH$.

By distilling methyl alcohol with a mixture of salt, nitre, and sulphuric acid, *chlorpicrin*, or *nitrochloroform*, $CCl_3(NO_2)$, is obtained. It is a colorless liquid boiling at 112°, with a piercing odor. Its vapors cause weeping. Nascent hydrogen converts it into methylamine.

Nitroform, $CH(NO_2)_3$, is produced by the action of water on trinitromethylcyanide. It forms cubical crystals, with a bitter taste and unpleasant odor, which fuse at 15°, and explode violently when heated suddenly. Treated with a mixture of sulphuric and nitric acids there is formed

Tetra-nitromethane $C(NO_2)_4$, a liquid solidifying at 13° and boiling at 126°. It is neither combustible nor explosive.

Fulminic acid, nitrocyanmethane, $CN^-CH_2NO_2$. The acid does not exist in the free state, but its salts are well known, and the mercuric fulminate, in particular, is used as an explosive (percussion caps, etc.). *Mercuric fulminate* is produced by adding alcohol to a solution of mercury in nitric acid. It separates in prismatic crystals, which explode violently when struck. *Silver fulminate* can be obtained in a similar manner. By boiling mercuric fulminate with potassium or ammonium chloride, salts of *fulminuric acid,* $C_3H_3N_3O_3$, an acid isomeric with cyanuric, are formed.

The further substitutions, *dinitrocyanmethane,* $CN^-CH(NO_2)_2$, and *trinitrocyanmethane,* $CN^-C(NO_2)_3$, are also known.

Phosphorus Derivatives.

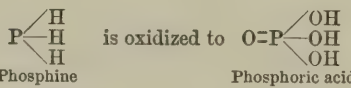
There are compounds analogous to the amines, in which instead of the tri-valent nitrogen, we have a tri-valent phosphorus. Such compounds are called *phosphines.* They do not possess the marked basic properties of the amines, *i.e.*, they do not combine so easily with acids to form salts, in fact the hydrogen phosphide, from which they are derived in the same manner as the amines from ammonia, has no tendency to form salts. The only salt that can be easily produced from it, phosphonium iodide, PH_4I, is energetically decomposed by water into iodohydric acid and hydrogen phosphide (phosphine). On the other hand, they have a strong tendency to oxidize, whereby the phosphorus passes from the tri-valent to the penta-valent state. Phosphines are formed by the action of hydrogen phosphide on alkylogens, the reaction being analogous to the formation of amines from ammonia:

$$CH_3I + PH_3 = CH_3PH_2 \,.\, HI,$$
$$2\,CH_3I + 2\,PH_3 = (CH_3)_2PH \,.\, HI + PH_4 \,.\, I.$$

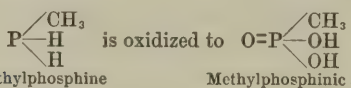
Phosphonium iodide also acts on the alkylogens, iodohydric acid being split off:

$$CH_3I + PH_4I = CH_3PH_2 \,.\, HI + HI.$$

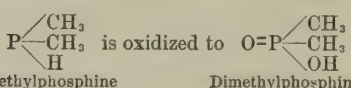
The peculiar compounds formed by the oxidation of the phosphines are called *phosphinic acids.* The oxidation of the phosphines is easily understood when the fact is recalled that hydrogen phosphide is easily oxidized to phosphoric acid. The process of oxidation is the same in case of a phosphine, except that in the case of hydrogen phosphide all the H's are oxidized to OH's, while in the phosphines the alkyl substitution is not oxidized :



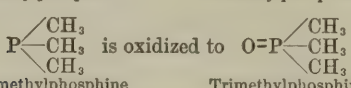
Phosphine — Phosphoric acid



Methylphosphine — Methylphosphinic acid



Dimethylphosphine — Dimethylphosphinic acid



Trimethylphosphine — Trimethylphosphinic oxide

Phosphoric acid is a tribasic acid, methylphosphinic acid is a dibasic acid, dimethyl-phosphinic acid is a monobasic acid ; trimethylphosphinic oxide is not an acid since it contains no hydroxyl.

The oxidation is easily effected by means of fuming nitric acid.

The phosphines are colorless liquids with unpleasant odors and strong refractive powers. They oxidize easily when exposed to the air, often taking fire, particularly when warm. Hence during their production and distillation the air must be kept excluded from them.

Methylphosphine, CH_3PH_2. At ordinary temperatures it is a colorless gas with a very unpleasant odor somewhat resembling hydrogen phosphide. By leading it into concentrated iodohydric acid, *methyl-phosphonium iodide,* $CH_3(PH_2)HI$, is obtained in white rhombohedrons which are decomposed by water into their constituents. Fuming nitric acid converts it into the dibasic *methyl-phosphinic acid,* $CH_3PO(OH)_2$.

Dimethylphosphine, $(CH_3)_2PH$, is a colorless liquid boiling at 25°. It has a very disagreeable odor, and ignites when exposed to the air. Fuming nitric acid converts it into the mono-basic *dimethylphosphinic acid.*

Trimethylphosphine, $(CH_3)_3P$, is produced by the action of phosphorus trichloride on zinc methyl :

$$2\,PCl_3 + 3\,(CH_3)_2Zn = 2\,(CH_3)_3P + 3\,ZnCl_2.$$

Colorless, strongly refractive liquid boiling at 40°. It unites easily with oxygen to $(CH_3)_3PO$, with chlorine to $(CH_3)_3PCl_2$, with bromine to $(CH_3)_3PBr_2$, with sulphur to $(CH_3)_3PS$, with selenium, etc.

Trimethylphosphine unites with methyl iodide to form

Tetra-methyl-phosphonium iodide, $(CH_3)_4PI$, which by the action of silver oxide is converted into

Tetra-methyl-phosphonium hydroxide, $(CH_3)_4POH$.

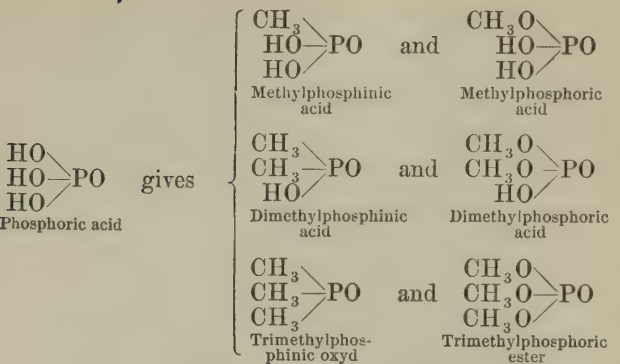
The analogies of the two series appear very distinctly on comparison with the amines.

A compound is also known to which there is no corresponding nitrogen compound. Its constitution is analogous to that of *methyl hydrazin*, $(CH_3)_2N{-}NH_2$. It is derived from the liquid hydrogen phosphide, and is called

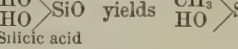
Phosphorus dimethyl, $(CH_3)_4P_2$. Its constitution is either $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!P{-}P\!<\!\!\begin{matrix}CH_3\\CH_3\end{matrix}$ derived from tri-valent phosphorus, or $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!P{\equiv}P\!<\!\!\begin{matrix}CH_3\\CH_3\end{matrix}$ from penta-valent phosphorus. Colorless, oily liquid boiling at 25°.

The phosphinic acids are derived from phosphoric acid in the same manner as the nitro-compounds from nitric acid and the sulphonic acids from sulphuric acid. In these compounds the *hydroxyl* of the acid is replaced by hydrocarbon rests, while in the esters, or compound ethers, only the hydrogen of the acid is replaced:

$HO{-}NO_2$ Nitric acid	gives	$CH_3{-}NO_2$ Nitromethane	and	$CH_3{-}O{-}NO_2$ Methylnitric ester
$\begin{matrix}HO\\HO\end{matrix}\!\!>\!SO_2$ Sulphuric acid	gives	$\begin{matrix}CH_3\\HO\end{matrix}\!\!>\!SO_2$ Methylsulphonic acid	and	$\begin{matrix}CH_3O\\HO\end{matrix}\!\!>\!SO_2$ Methylsulphuric acid
		$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!SO_2$ Methylsulphone	and	$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!\!>\!SO_2$ Methylsulphuric ester



In the same manner, a hydroxyl of silicic acid can be replaced by alkyl rests :



This compound, CH_3SiOOH, on account of the tetra-valence of the silicon, has been considered as acetic acid in which the carbon of the carboxyl group has been replaced by a silicon atom, and it has hence been called *silico-acetic acid.*

Arsenic Derivatives.

The methyl- and dimethyl-arsine derivatives of the tri- and penta-valent arsenic are not yet known. Analogous compounds have been produced, however, in which the hydrogen of the hydrogen arsenide is replaced by chlorine.

Monomethyl-arsenic dichloride, CH_3AsCl_2, liquid boiling at 133°. With chlorine it unites to *monomethyl-arsenic tetrachloride*, CH_3AsCl_4.

Dimethyl-arsenic chloride, $(CH_3)_2AsCl$, liquid boiling at about 100°. By the action of chlorine it forms *dimethyl-arsenic trichloride*. $(CH_3)_2AsCl_3$.

Trimethyl-arsine, $(CH_3)_3As$. Colorless liquid with an offensive odor, boiling at 120°. It unites with chlorine, bromine, iodine, oxygen, sulphur, etc., in the same manner of trimethylphosphine.

Tetramethyl-arsonium iodide, $(CH_3)_4AsI$.

Tetramethyl-arsonium hydroxide, $(CH_3)_4AsOH$.

The most important arsenic compound of methyl is

Arsenic dimethyl, cacodyl, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!As\text{-}As\!<\!\!\begin{matrix}CH_3\\CH_3\end{matrix}$, or $(CH_3)_4As_2$. It is produced by the distillation of equal parts of dry potassium acetate and arsenous anhydride. It is a liquid with an extremely disagreeable odor, boiling at 170°. When exposed to the air it fumes and ignites. By the slow action of oxygen, cacodyl oxide and cacodylic acid are formed.

Cacodylic oxide, alcarsine, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!As\text{-}O\text{-}As\!<\!\!\begin{matrix}CH_3\\CH_3\end{matrix}$, is the chief product of the above distillation of potassium acetate and arsenous anhydride. It is an oil with an offensive odor, boiling at 150°. Exposed to the air it does not fume, but oxidizes slowly to

Cacodylic acid, dimethyl-arsinic acid, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!AsO(OH)$. Large, odorless, deliquescent prisms, fusing at 200°. Its salts are crystalline. It corresponds to the dimethylphosphinic acid.

Methylarsinic acid, $CH_3AsO(OH)_2$, corresponding to methylphosphinic acid, is also known, and is produced by the action of silver oxide on methyl arsenic dichloride, CH_3AsCl_2.

All of these arsenic derivatives are made from cacodyl.

Antimony Derivatives.

The compounds of methyl with tri- and penta-valent antimony possess still less basic character than the preceding derivatives.

Trimethyl-stibine, $(CH_3)_3Sb$, obtained by the action of potassium antimonide on methyl iodide:

$$K_3Sb + 3\,CH_3I = 3\,KI + (CH_3)_3Sb.$$

Colorless liquid boiling at 86°. With methyl iodide it unites to

Tetramethyl-stibonium iodide, $(CH_3)_4SbI$, a hard crystalline mass which yields with moist silver oxide.

Tetramethyl-stibonium hydroxide, $(CH_3)_4Sb\text{-}OH$, white, deliquescent crystalline mass with strong basic properties.

Trimethylstibine iodide, $(CH_3)_3SbI_2$. Obtained by digestion of metallic antimony with methyl iodide. It crystallizes in needles or prisms.

In a similar manner *trimethyl bismuthine*, $(CH_3)_3Bi$, is obtained by the action of methyl iodide on potassium bismuthide. The methyl com-

pound of boron, *trimethyl borine*, $(CH_3)_3B$, is also known. It is a colorless gas, with a sharp, peculiar odor.

Compounds of Methyl with Metals.

1) By the digestion of finely granulated zinc with methyl iodide, *methyl-zinc iodide*, CH_3ZnI, a crystalline compound, is obtained, which, by distillation, falls into zinc iodide and zinc methyl:

$$2\,CH_3ZnI = (CH_3)_2Zn + ZnI_2.$$

Zinc methyl is a colorless liquid boiling at 46°. It has an unpleasant odor. When exposed to the air, it ignites and burns with a greenish-blue flame. Water decomposes it immediately into methane and zinc hydroxide:

$$(CH_3)_2Zn + 2\,H_2O = 2\,CH_4 + Zn(OH)_2.$$

2) By the action of methyl iodide on mercury, a crystalline compound, *methyl-mercury iodide*, CH_3HgI, is obtained, while by the action of methyl iodide on mercury amalgam, *mercury methyl*, $(CH_3)_2Hg$, is formed:

$$2\,CH_3I + Na_2Hg = (CH_3)_2Hg + 2\,NaI.$$

Colorless liquid insoluble in water, boiling at 95°, and easily combustible. Its vapors are very poisonous.

3) Methyl iodide and magnesium filings give *magnesium methyl*, $(CH_3)_2Mg$, a liquid which has a strong odor and ignites on exposure to the air.

4) By the action of zinc methyl on silicium chloride, *tetramethyl-silicium*, $(CH_3)_4Si$, is produced:

$$2\,(CH_3)_2\,Zn + SiCl_4 = (CH_3)_4Si + 2\,ZnCl_2.$$

Colorless, easily combustible liquid, boiling at 30°.

5) Methyl iodide and an alloy of tin and sodium yield *tin tetramethyl*, $Sn(CH_3)_4$. It is a liquid with an ethereal odor, boiling at 78°.

6) Lead chloride and zinc methyl give *lead tetramethyl*, $Pb(CH_3)_4$. This compound proves the tetra-valence of lead.

In conclusion, we will consider briefly some of the organic salts, or esters, of methane.

The method of producing methylsulphuric acid and methyl sulphuric ester have already received a passing notice. The methylsulphuric acid is formed by mixing carefully methyl alcohol and sulphuric acid. The excess of sulphuric acid is

removed by adding barium carbonate to the mixture diluted with water. Barium sulphate is formed and separates, while the methylsulphuric acid is transformed into the easily soluble barium salt. The barium sulphate is removed by filtration, and the barium methylsulphate obtained by evaporation of the solution. From the latter the methylsulphuric acid is set free by sulphuric acid. In the free state it is but little known. It forms long,deliquescent needles, and its aqueous solution on heating breaks into methyl alcohol and sulphuric acid :

$$\begin{matrix}CH_3O\\HO\end{matrix}\!\!\rangle SO_2 + H_2O = \begin{matrix}HO\\HO\end{matrix}\!\!\rangle SO_2 + CH_3(OH).$$

It is a monobasic acid, and forms with metals finely crystallizing salts, which are easily soluble. Its potassium and barium salts are frequently used instead of methyl iodide, bromide, or chloride for the production of other derivatives of methane, since the rest SO_4H is easily substituted. By distillation of potassium methylsulphate with potassium cyanide, for instance, methyl cyanide and potassium sulphate are formed :

$$\begin{matrix}CH_3O\\KO\end{matrix}\!\!\rangle SO_2 + KCN = CH_3CN + \begin{matrix}KO\\KO\end{matrix}\!\!\rangle SO_2 \text{ or } K_2SO_4.$$

Methyl Sulphuric Ester, $\begin{matrix}CH_3O\\CH_3O\end{matrix}\!\!\rangle SO_2$, is formed by the distillation of a mixture of 1 part of methyl alcohol with 8 parts of sulphuric acid. It is a colorless liquid boiling at 188°, and has the odor of garlic.

Methyl Nitric Ester, CH_3ONO_2, is formed by the distillation of nitre and methyl alcohol with sulphuric acid. It is a liquid with an ethereal odor, boiling at 66°, which at a higher temperature (150°) explodes violently.

Methylboric ester, $\begin{matrix}CH_3O\\CH_3O\\CH_3O\end{matrix}\!\!\rangle Bo$, is formed by the action of boron trichloride on methyl alcohol :

$$BoCl_3 + 3\,CH_3OH = (CH_3O)_3Bo + 3\,HCl.$$

Colorless liquid boiling at 72°. With water it breaks into boracic acid and methyl alcohol:

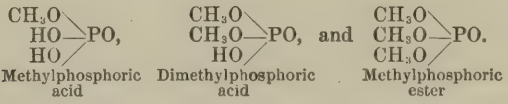
$$(CH_3O)_3Bo + 3\,H_2O = 3\,CH_3OH + Bo(OH)_3.$$

Methyl silicic ester, $(CH_3O)_4Si$, is produced from silicon chloride and methyl alcohol:

$$4\,CH_3OH + SiCl_4 = (CH_3O)_4Si + 4\,HCl.$$

Colorless liquid with an ethereal odor, b. p. 124°. With water it decomposes after some time into silicic acid and methyl alcohol.

The three esters of phosphoric acid with methyl have already been mentioned:



Methylphosphoric acid — Dimethylphosphoric acid — Methylphosphoric ester

The compounds which have thus far been considered contain only one atom of carbon, or contain several atoms of carbon which are not directly connected, as, for instance, methyl ether, $H_3C^-O^-CH_3$, and trimethylamine, $\begin{matrix} H_3C^-N^-CH_3 \\ | \\ CH_3 \end{matrix}$. Only two compounds have been mentioned in which carbon is united to carbon. These were cyan, $\begin{matrix} CN \\ | \\ CN \end{matrix}$, and cyanmethane, or aceto-nitrile, $\begin{matrix} CH_3 \\ | \\ CN \end{matrix}$. These were considered in this group in order not to lose sight of their relation. We come now to the great classes of compounds which contain several atoms of carbon directly united.

We can imagine a hydrogen atom of methane to be replaced by the methyl group, thus forming the compound, $CH_3^-CH_3$, dimethyl, from which derivatives may be produced in the same manner as the methyl compounds from methane.

C_2 GROUP.

Ethane Compounds.

Hydrocarbons.

1) The two carbon atoms are united by a simple binding.

Ethane, *Dimethyl,* $CH_3{-}CH_3$, C_2H_6, is formed by the action of water on zinc-ethyl :

$$(C_2H_5)_2Zn + 2\,H_2O = 2\,C_2H_6 + Zn(OH)_2.$$

Or by the electrolysis of acetic acid :

$$2\,CH_3{-}COOH = C_2H_6 + 2\,CO_2 + H_2.$$

It is a colorless gas, burning with a faintly luminous flame. By the action of chlorine the hydrogens are substituted by it :

$$CH_3{-}CH_3 + Cl_2 = \underset{\text{Ethyl chloride}}{CH_3{-}CH_2Cl} + HCl.$$

2) The two carbon atoms are united by a double binding.

Ethylene, *Olefiant Gas,* $CH_2{=}CH_2$, C_2H_4.

It is produced by heating 1 part of alcohol with 6 parts of concentrated sulphuric acid. The elements of a molecule of water are extracted from the alcohol, (predisposing affinity).

$$CH_3{-}CH_2OH = CH_2{=}CH_2 + H_2O.$$

It is a colorless, poisonous gas, with an unpleasant, suffocat-

ing odor, burning with a luminous flame. It combines directly with chlorine, bromine, and iodine :

$$CH_2{=}CH_2 + Cl_2 = CH_2Cl{-}CH_2Cl.$$

In the presence of platinum black it unites with hydrogen to ethane :

$$CH_2{=}CH_2 + H_2 = CH_3{-}CH_3.$$

With oxygen it forms a compound, ethylene oxide, $H_2C{-}CH_2$ (O), which is isomeric with aldehyde, $CH_3{-}CHO$.

3) The two carbon atoms are united by a triple binding.

Acetylene, $CH{\equiv}CH$, C_2H_2.

It is formed directly from its elements, when electric sparks are passed between carbon poles in an atmosphere of hydrogen. It is also produced when organic bodies are exposed to a high heat, *e.g.*, when methane, alcohol, ether, etc., are passed through heated tubes, or when organic substances (ether, benzene,) are burnt with an insufficient supply of oxygen. It is present in small amounts in illuminating gas. It is made by boiling ethylene bromide with alcoholic potash :

$$C_2H_4Br_2 + 2\,KOH = C_2H_2 + 2\,KBr + 2\,H_2O.$$

Or by passing ethylene chloride over heated lime.

Acetylene is a colorless gas with a strongly offensive odor, burning with a luminous smoky flame. With nascent hydrogen it unites to ethylene. It combines directly with the halogens, forming $C_2H_2Cl_2$ and $C_2H_2Cl_4$, etc.

A characteristic property of this compound is its absorption by an ammoniacal solution of cuprous chloride, Cu_2Cl_2, or silver nitrate solution, $AgNO_3$. In the former case a red precipitate, $C_2Cu_2 + H_2O$, is formed, while in the latter a brown substance, $C_2Ag_2 + H_2O$, is precipitated Both of these compounds explode by heating or percussion.

By leading acetylene over melted potassium, hydrogen is evolved, and the compounds C_2HK and C_2K_2 are formed. In the presence of platinum-black, acetylene unites with hydrogen to ethane.

Halogen Substitutions of Ethane.

Ethyl Chloride, *Monochlorethane,* $CH_3{}^-CH_2Cl$, or C_2H_5Cl, is formed by the action of chlorine on ethane. It is made by the action of gaseous chlorhydric acid on ethyl alcohol. It is a colorless liquid with a pleasant odor, boiling at 12°. Chlorine acts on it, forming higher substitution products. As has already been explained in the Introduction (p. 10), the higher substituted halogen derivatives of ethane, owing to the distribution of the chlorine atoms, form two isomeric series.

Ethyl Bromide, *Monobromethane,* $CH_3{}^-CH_2Br$, or C_2H_5Br.

It is produced by digesting ethyl alcohol with gaseous bromhydric acid, or by dropping bromine into alcohol containing melted phosphorus.

It is a colorless liquid with a pleasant odor, boiling at 39°.

Ethyl Iodide, *Mono-iodo-ethane,* $CH_3{}^-CH_2I$, or C_2H_5I.

To 1 part of amorphous phosphorus in 5 parts of alcohol, 10 parts of iodine are carefully added, the whole allowed to stand 24 hours and then distilled.

It is a colorless liquid boiling at 72°. On exposure to the light it gradually turns brown.

Ethylene Chloride, *Ethene Chloride, Dichlorethane, Dutch Liquid,* $CH_2Cl^-CH_2Cl$. This substance is formed by exposing a mixture of chlorine and ethylene to sunlight. It is made by passing equal parts of chlorine and ethylene into boiling antimony pentachloride. It is a liquid with an odor resembling chloroform. It boils at 85°. With alcoholic potash it splits off HCl :

$$CH_2Cl^-CH_2Cl + KHO = CH_2{}^=CHCl + KCl + H_2O.$$

Isomeric with it is

Ethylidene Chloride, *Ethidene Chloride, Chlorethylidene, Chlorethidene,* $CH_3{}^-CHCl_2$, or $C_2H_4Cl_2$. It is obtained as the

first product of the action of chlorine on ethyl chloride. Colorless liquid with a pleasant odor, boiling at 57.5°.

Mono-chlor-ethylene chloride, $CH_2Cl{=}CHCl_2$. Liquid boiling at 115°. With alcoholic potash, an HCl splits out:

$$CH_2Cl{=}CHCl_2 + KOH = CHCl{=}CHCl + KCl + H_2O.$$

Mono-chlor-ethylidene chloride, methyl chloroform, $CH_3{-}CCl_3$, or $C_2H_3Cl_3$. Boils at 75°. Alcoholic potash converts it into the acetate:

$$CH_3{-}CCl_3 + 4\,KOH = CH_3{-}COOK + 3\,KCl + 2\,H_2O.$$

Dichlorethylene chloride, dichlorethene chloride, $CH_2Cl_2{-}CHCl_2$, boils at 147°, and by the action of KOH is converted into

Dichlorethylidene chloride, dichlorethidene chloride, $CH_2Cl{-}CCl_3$, or $C_2H_2Cl_4$. Boils at 127.5°. By the action of alcoholic KOH, $CHCl{-}CCl_3$ is also formed.

Pentachlorethane, $CCl_3{-}CHCl_2$. Boils at 158°.

Perchlorethane, hexachlorethane, C_2Cl_6, is the final product of the action of chlorine on ethyl chloride. It crystallizes in well-formed rhombic crystals, which fuse at 185°, but boil at 184°, so that under the ordinary atmospheric pressure it sublimes without melting. By the action of weak reducing agents, as potassium sulphydrate, it falls into C_2Cl_4 and Cl_2. We see from the foregoing that alcoholic potash converts the higher chlorine derivatives of ethane into chlorinated ethylenes with elimination of HCl.

The following is a list of the chlorine derivatives of ethane:

Ethyl chloride	$CH_3{-}CH_2Cl$	B. p. 12°
Ethylene chloride	$CH_2Cl{-}CH_2Cl$	B. p. 85°
Ethidene chloride	$CH_3{-}CHCl_2$	B. p. 57.5°
Mono-chlorethylene chloride . .	$CH_2Cl{-}CHCl_2$	B. p. 115°
Mono-chlorethidene chloride .	$CH_3{-}CCl_3$	B. p. 75°
Di-chlorethylene chloride . . .	$CHCl_2{-}CHCl_2$	B. p. 147°
Dichlorethidene chloride . . .	$CH_2Cl{-}CCl_3$	B. p. 127.5°
Pentachlorethane	$CHCl_2{-}CCl_3$	B. p. 158°
Perchlorethane	$CCl_3{-}CCl_3$	B. p. 184°

Ethylene Bromide, $CH_3{-}CH_2Br$, or C_2H_5Br, is obtained by shaking ethylene with bromine. It is a crystalline substance, fusing at 9° and boiling at 129°.

Ethylidene bromide, ethidene bromide, $CH_3{}^-CHBr_2$, or $C_2H_4Br_2$, is obtained from aldehyde, C_2H_4O, and phosphorus bromide. Colorless liquid boiling at 114°.

Ethylene iodide, $CH_2I{}^-CH_2I$, or $C_2H_4I_2$, is produced by the union of ethylene and iodine. Colorless crystals turning rapidly yellow. Fuses at 73°.

Ethylene also yields substitution products.

Monochlorethylene, $CH_2{=}CHCl$, is formed by the action of potassium hydroxide solution on ethylene chloride. Boils at −18°.

Dichlorethylene, $CHCl{=}CHCl$, is made from monochlorethylidene chloride. It boils at 37°.

Trichlorethylene, $CHCl{=}CCl_2$. Boils at 87°.

Tetrachlorethylene, $CCl_2{=}CCl_2$. It is formed from C_2Cl_6 and KSH. Boils at 117°.

The corresponding bromine and iodine derivatives are known, and are formed by reactions analogous to the chlorides.

Hydroxyl Substitutions of Ethane.

Ethyl Alcohol, Alcohol par excellence, *Spirit of Wine*, $CH_3{}^-CH_2{}^-OH$, or C_2H_6O. Alcohol forms the starting-out point for the production of all ethyl compounds. It is made commercially by fermenting grape sugar (glucose) with yeast, as will be described under sugar. The dextrose breaks into alcohol and carbonic acid:

$$C_6H_{12}O_6 = 2\,C_2H_6O + 2\,CO_2.$$

Alcohol is made from materials containing starch (rye, rice, potatoes, corn, etc.), or sugar (beet-root molasses). Both the starch and the sugar are first converted into glucose by addition of the elements of water:

$$\underset{\text{Starch}}{C_6H_{10}O_5} + H_2O = \underset{\text{Grape sugar}}{C_6H_{12}O_6}$$

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O = 2\,\underset{\text{Grape sugar}}{C_6H_{12}O_6}.$$

In the fermentation of glucose, small amounts of alcohols of the higher carbon series are formed, particularly amyl alcohol, but in quantities so small that they can be omitted from the formula.

By distilling the product of the fermentation, alcohol is obtained mixed with water. As the boiling point of alcohol is considerably under that of water, the alcohol can be freed from the water as well as from the accompanying impurities, which injure its taste, by redistilling in a special form of apparatus. In this manner a distillate is obtained containing about 93% alcohol and 7% water. This alcohol is used in the arts. To prepare absolute alcohol, it is allowed to stand a week or more over burnt lime and then redistilled. The last traces of water can be removed by metallic sodium.

Alcohol is a colorless, mobile liquid with a pleasant odor, boiling at 78.5°. Its sp. gr. at 15° is 0.79. At − 100° it becomes thick but does not solidify.

It has a burning taste and is poisonous. When injected into the veins, it causes death in a short time. Moisture is attracted by it with such avidity that it extracts the water of crystallization from many salts, *e.g.* sodium sulphate. It is combustible, burning with a bluish, slightly luminous flame.

It dissolves essential oils, resins, fats, bromine, iodine, and sulphur and phosphorus in small amounts.

As the value of alcoholic liquids depends on their content of alcohol, the amount of alcohol can be estimated, when they consist of only alcohol and water, by taking the specific gravity of the liquid. Tables have been made which show the specific gravity of mixtures of alcohol and water. Thus a mixture of 1% alcohol and 99% of water has the specific gravity 0.9985. Since alcohol, however, expands or contracts strongly with increasing or decreasing temperatures, the table only holds good for a specified temperature (15°). If the temperature is different from that given, the specific gravity must be corrected. Tables have also been made for this purpose, which give the true value between 12° and 38°. A 60% alcohol, for instance, at −10°, shows 57.4%, and at + 30°, 68.5%. For the estimation of the per cent. of alcohol by means of specific gravity, both tables are therefore necessary. If the liquid contains other matters in solution, as is the case in wine and beer, about half of the liquid must be distilled off, the alcohol estimated in the distillate, and the per cent. calculated for the whole.

Alcohol can be produced synthetically from its elements.

By passing electric sparks between carbon poles in an atmosphere of hydrogen, the carbon unites with hydrogen to form acetylene, $CH{\equiv}CH$, which combines with hydrogen, producing ethylene, $CH_2{=}CH_2$. Ethylene with sulphuric acid yields ethyl-sulphuric acid :

$$CH_2{=}CH_2 + H_2SO_4 = CH_3{-}CH_2HSO_4,$$

which by the action of potassium hydroxide is transformed into alcohol :

$$CH_3{-}CH_2HSO_4 + 2\,KHO = CH_3{-}CH_2OH + K_2SO_4 + H_2O.$$

Ethyl alcohol unites with various salts forming crystalline compounds, as $CaCl_2$, $4\,C_2H_6O$. The alkali metals, K and Na, dissolve in alcohol with evolution of hydrogen, forming ethoxides, or alcoholates :

$$C_2H_5{-}OH + K = \underset{\text{Potassium ethoxide}}{C_2H_5{-}OK} + H.$$

When mixed with concentrated sulphuric acid, alcohol becomes strongly heated, forming ethyl-sulphuric acid :

$$C_2H_6O + H_2SO_4 = C_2H_5HSO_4 + H_2O,$$

which gives salts with metals. On boiling with water, it is decomposed into sulphuric acid and water:

$$C_2H_5HSO_4 + H_2O = C_2H_5{}^{-}OH + H_2SO_4.$$

In the same manner, its salts are decomposed by boiling with water into primary sulphate and alcohol:

$$C_2H_5KSO_4 + H_2O = C_2H_5OH + KHSO_4.$$

(Compare methyl alcohol.)

Isethionic acid, or hydroxyethylsulphonic acid, $\begin{matrix}CH_2(OH)\\ |\\ CH_2HSO_3\end{matrix}$, is isomeric with ethylsulphuric acid, and is obtained by treating ethylene, ether, or alcohol with sulphuric anhydride and boiling the product with water. Its salts are easily crystallizable. It is a sulphonic acid, *i.e.*, the sulphur of the group SO_3H is bound directly to the carbon. Ammonium isethionate, when heated to 200°, loses the elements of water, forming *amidoethylsulphonic acid, taurine,* $\begin{matrix}CH_2(NH_2)\\ |\\ CH_2{}^{-}SO_3H\end{matrix}$. Taurine occurs in nature, and is found combined with cholic acid in the bile. It forms colorless, transparent, hexagonal prisms, soluble in water, insoluble in alcohol and ether. It is very stable toward acids, but is decomposed on boiling with alkalis. Nitrous acid converts it back into isethionic acid:

$$\begin{matrix}CH_2NH_2\\ |\\ CH_2SO_3H\end{matrix} + HNO_2 = \begin{matrix}CH_2(OH)\\ |\\ CH_2SO_3H\end{matrix} + H_2O + N_2.$$

The compound of aldehyde with ammonia and sulphurous acid is isomeric with taurine:

$$\begin{matrix}CH_3\\ |\\ CH\end{matrix} \begin{matrix}NH_2\\ SO_3H.\end{matrix}$$

With calcium hypochlorite, alcohol yields chloroform; with chlorine, chloral. Oxidizing agents convert alcohol into aldehyde and acetic acid.

With acids, alcohol forms organic salts, or esters.

Nitric ethyl ester, ethyl nitrate, $C_2H_5{}^-O{}^-NO_2$, is made by the distillation of 2 vols. of alcohol and 1 vol. of nitric acid (1.4 sp. gr.), with the addition of a small amount of urea to prevent the formation of nitrous acid. It is a colorless liquid, boiling at 87°.

Nitrous ethyl ester, ethyl nitrite, nitrous ethyl ether, $C_2H_5{}^-O{}^-NO$, is obtained by leading nitrous acid into alcohol. If a mixture of alcohol and nitric acid is distilled without the addition of urea, nitrous ester is chiefly obtained, because, owing to the reducing action of the alcohol, the nitric acid is reduced to nitrous acid, in which state it acts on the remaining alcohol.

The spirits of niter sold in the drug stores is a solution of nitrous ethyl ester in alcohol, and is prepared by distilling alcohol with nitric acid.

Nitrous ethyl ester is a colorless liquid with a pleasant odor, boiling at 16.5°, and soluble in 40 parts of water.

Ether, Sulphuric Ether, *Ethyl Oxide,* $C_2H_5{}^-O{}^-C_2H_5$, or $C_4H_{10}O$.

The general method of the formation of ethers has been described under methyl alcohol. Ethyl ether is made by heating 9 parts of sulphuric acid with 5 parts of alcohol of 90% to 135°-140°. The apparatus is so constructed that the alcohol flows in continually, for in the formation of ether the sulphuric acid is constantly regenerated. At first ethylsulphuric acid is formed :

$$C_2H_6O + H_2SO_4 = C_2H_5HSO_4 + H_2O.$$

The ethylsulphuric acid is decomposed by a second molecule of alcohol at 140° into ether and free sulphuric acid. The reaction is analogous to the decomposition of this acid into alcohol and sulphuric acid by water :

$$C_2H_5HSO_4 + HOH = C_2H_5OH + H_2SO_4,$$
$$C_2H_5HSO_4 + C_2H_5OH = C_2H_5OC_2H_5 + H_2SO_4.$$

At this temperature the ether and water distil off, so that there remains always concentrated sulphuric acid for the decomposition of a fresh portion of alcohol.

The ether is freed from alcohol by washing with water, and from moisture by means of caustic lime. It is a colorless, very mobile liquid, with a pleasant odor and burning taste. Sp. gr. at 0° is 0.736. It boils at 35°, is easily combustible, and burns with a luminous flame.

Ether is miscible with alcohol, and dissolves $\frac{1}{36}$ of its volume of water. When inhaled, it causes intoxication, and then loss of consciousness and sensation. It is used to produce insensibility during painful surgical operations.

Chlorine acts on ether, replacing hydrogen. In this manner there are obtained :

Monochlor-ether, C_4H_9ClO, colorless liquid boiling at 97–98°.
Dichlor-ether, $C_4H_8Cl_2O$, liquid boiling at about 145°.
Tetrachlor-ether, $C_4H_6Cl_4O$, an oil boiling at 190°.
Perchlor-ether, $C_4Cl_{10}O$, crystals melting at 69°.

The constitution of monochlor-ether is : $CH_3CHCl^-O^-CH_2^-CH_3$,
of dichlor-ether : $CH_2Cl^-CHCl^-O^-CH_2^-CH_3$,
of tetrachlor-ether : $CCl_3^-CHCl^-O^-CH_2^-CH_3$.

Ether forms with bromine an easily crystallizable compound fusing at 22°.

Methyl-ethyl-ether, $CH_3^-O^-C_2H_5$. Liquid boiling at 11°. Its properties are analogous to those of ethyl ether. It is an example of a mixed ether (p. 28).

Aldehyde, Acetaldehyde, CH_3^-CHO, or C_2H_4O. Aldehyde is formed by the oxidation of alcohol. It can be made by the action of chromic acid on alcohol.

It is obtained as a side product in the manufacture of spirits. In rectifying the alcohol, various impurities, which are but little understood, but which, besides the fusel oil, impart a disagreeable odor to the alcohol, have to be removed by oxidation. To effect this, the spirit is passed through a series of charcoal filters, which exert an oxidizing action owing to the oxygen condensed in the pores of the charcoal. A portion of the alcohol is, however, also oxidized. From this portion, which goes over first in the distillation and is kept apart, the aldehyde is obtained by fractional distillation.

Aldehyde is a colorless, very mobile liquid, with a suffocating odor. It boils at 21°. Its sp. gr. is 0.8. With alcohol and water it is miscible with elevation of temperature, and is soluble in ether in all proportions. It is combustible.

Characteristics of the Aldehydes.

1) Aldehydes exert a reducing action because they are easily oxidized into their corresponding acids. They decompose silver salts, setting the silver free. As the reduction takes place without the evolution of gas, the silver is deposited on the sides of the glass as a brilliant film. *Aldehydes produce what is called a silver mirror.*

2) The acid sulphites of the alkalis give difficultly soluble crystalline compounds with the aldehydes :

$$C_2H_4O + NaHSO_3 = C_2H_4O \,.\, NaHSO_3.$$

3) Potassium or sodium hydroxide converts them into resins, (aldehyde resin).

4) Aldehydes are formed from the corresponding acids by distilling their salts with a formate :

$$\underset{\text{Sodium acetate}}{CH_3{}^-COONa} + \underset{\text{Sodium formate}}{HCOONa} = \underset{\text{Aldehyde}}{CH_3{}^-CHO} + Na_2CO_3.$$

5) Aldehydes are easily converted into acids :

$$C_2H_4O + O = C_2H_4O_2.$$

6) With nascent hydrogen (sodium amalgam), aldehydes pass into their alcohols :

$$C_2H_4O + H_2 = C_2H_6O.$$

7) The aldehydes polymerize easily.

8) Aldehydes unite with ammonia and cyanhydric acid, the double oxygen binding being broken :

$$CH_3{}^-CHO + NH_3 = CH_3{}^-CH\begin{matrix}OH\\NH_2\end{matrix}.$$

$$CH_3{}^-CHO + HCN = CH_3{}^-CH\begin{matrix}OH\\CN\end{matrix}.$$

If ammonia gas is passed into an ethereal solution of aldehyde, there is formed :

Aldehyde-ammonia, $CH_3{-}CH\langle^{OH}_{NH_2}$, or C_2H_7NO, which crystallizes in rhombohedrons, and distils at 100°. By the action of acids, aldehyde is set free.

Hydrogen sulphide converts aldehyde-ammonia into *thialdine*, $C_6H_{13}NS_2$:

$$3\,C_2H_7NO + 3\,H_2S = C_6H_{13}NS_2 + (NH_4)_2S + 3\,H_2O.$$

Aldehyde when treated with potassium hydroxide solution is converted into a yellow resinous mass, *aldehyde resin*.

Aldehyde forms two polymeric modifications. 1) *Paraldehyde*, formed by the union of three molecules of aldehyde: $3\,C_2H_4O = C_6H_{12}O_3$, is a colorless liquid which solidifies when cooled and melts at 12°. It boils at 125°, and has an ethereal odor. 2) *Metaldehyde*, which is probably a union of six molecules of aldehyde, $6\,C_2H_4O = C_{12}H_{24}O_6$. It forms long glittering needles which sublime at 115° without fusing, decomposing partly into the normal aldehyde. Heated at this temperature in a closed tube, it is entirely converted into aldehyde.

When aldehyde is digested at 100° with a trace of chlorhydric acid, a molecule of water splits out of two molecules of the aldehyde, and a condensed aldehyde, *crotonic aldehyde*, is formed.

$$2\,C_2H_4O - H_2O = C_4H_6O.$$

An intermediate compound is formed here by the union of two molecules of aldehyde, $C_4H_8O_2 = CH_3{-}CH(OH){-}CH_2{-}CHO$, *aldol*. It is also formed by allowing a mixture of aldehyde and dilute chlorhydric acid to stand at a low temperature. At a higher temperature, and in the presence of chlorhydric acid, it splits out a molecule of water, passing into crotonic aldehyde.

As was explained under methylaldehyde, aldehyde is a decomposition product of an unstable body which breaks up as it is formed: $CH_3{-}CH\langle^{OH}_{OH}$:

$$CH_3{-}CH\langle^{OH}_{OH} - H_2O = CH_3{-}CHO.$$

Although this body, dihydroxyethylidene, is not stable, and is hence not known, its derivatives have been produced. Aldehyde-ammonia, for instance, is the amide of it, $CH_3{-}CH\langle^{NH_2}_{OH}$. The ethyl ether of it, $CH_3{-}CH\langle^{OC_2H_5}_{OC_2H_5}$, *acetal*, is also a well-characterized body. It is formed with aldehyde in the oxidation of alcohol, and is a colorless liquid with an ethereal odor, boiling at 104°. The acetic ester has been produced:

$$CH_2{-}CH\langle^{O{-}C_2H_3O}_{O{-}C_2H_3O} = C_6H_{10}O_4.$$

There are several chlorine substitution products derived from aldehyde, viz., *monochloraldehyde, dichloraldehyde, trichloraldehyde, or chloral.*

Chloral, $CCl_3{-}CHO$, or C_2HCl_3O, is obtained by the action of chlorine on 98% alcohol. The alcohol goes at first into aldehyde:

$$C_2H_6O + Cl_2 = C_2H_4O + 2\,HCl,$$

which is then further chlorinated:

$$C_2H_4O + 3\,Cl_2 = C_2HCl_3O + 3\,HCl.$$

Chloral is a colorless liquid, with a peculiar characteristic odor, boiling at 94°. It attracts moisture with avidity. When mixed with water, there is formed, under considerable elevation of temperature,

Chloral Hydrate, $CCl_3{-}CH\langle^{OH}_{OH}$, or $C_2HCl_3O + H_2O$. It crystallizes in white tablets, which, on distillation, are resolved into chloral and water. It is used to produce sleep.

Chloral also combines with alcohol, forming

Chloral-alcoholate, $CCl_3{-}CH\langle^{OH}_{OC_2H_5}$, or $C_2HCl_3O + C_2H_6O$. It crystallizes in long, white needles.

Alkalis decompose chloral into chloroform and formic acid:

$$CCl_3{-}CHO + KHO = CCl_3H + CHKO_2.$$

Chloral, in its reactions, behaves as an aldehyde. It unites with acid alkali sulphites to form crystalline compounds, reduces silver salts, is oxidized to trichloracetic acid, etc.:

$$CCl_3{}^-CHO + O = \underset{\text{Trichloracetic acid}}{CCl_3{}^-COOH}.$$

Chloral unites directly with cyanhydric acid to form *chloralcyan hydrate:*

$$CCl_3{}^-CH\begin{matrix}OH\\CN\end{matrix} = CCl_3{}^-CHO + HCN.$$

By the action of bromine on alcohol, *bromal* is formed, $CBr_3{}^-CHO$. It is a liquid boiling at 172°, with a penetrating odor. Alkalis decompose it into bromoform and formic acid. It unites with water to *bromal hydrate*, and in its chemical relations is analogous to chloral.

Acetic Acid, *Vinegar,* $CH_3{}^-COOH$, $C_2H_4O_2$. Like ethyl alcohol, which is the most important of all alcohols, acetic acid is the most important of all organic acids. It is found in the juices of many plants (as potash and soda salts), and in the secretions of the glands, etc. It is formed by the oxidation of alcohol and aldehyde, by the distillation of wood, and by treating methyl cyanide (acetonitrile) with potash :

$$CH_3{}^-CN + KOH + H_2O = CH_3{}^-COOK + NH_3.$$

It is produced commercially as follows :

1) *From alcohol.* 8–10% alcohol is allowed to trickle down slowly through beech-wood shavings moistened with acetic acid which are contained in large casks. A great surface is thus exposed to the oxidizing action of the air. Holes near the top and bottom of the casks allow of a free circulation of air. The temperature of the room in which the casks stand should be from 24°–30°. In order to completely oxidize the alcohol, it is passed through the shavings several times. The oxidation is, however, not a simple chemical process, but a species of fermentation caused by the acetic fungus (mycoderma aceti).

2) *From wood. Wood-vinegar.* Wood is heated to a red heat in iron cylinders. Gaseous products (illuminating gas, wood-gas), aqueous and tarry products are formed. The aqueous products contain, besides other substances, acetic acid and methyl alcohol. They are neutralized with

lime and distilled to dryness. The residue from the distillation is decomposed by an acid, and the acetic acid thus set free is distilled off.

Acetic acid is also produced from wine (wine-vinegar) and many fruits.

Absolute acetic acid (glacial acetic acid) is solid at a low temperature and fuses at 17°. At the ordinary temperature it is a colorless liquid with a penetrating odor, boiling at 118° and causing blisters on the skin. Its sp. gr. is 1.0553. It is miscible with water, alcohol, and ether, is strongly acid, and expels carbonic acid from its salts. It is monobasic and forms salts and esters.

The specific gravity of a weak acetic acid, such as vinegar, which is a 5%–15% aqueous solution of acetic acid, cannot be used as a means of determining the amount of pure acetic acid in it because an acid of 96% has the same specific gravity as one of 70%. The specific gravity of acetic acid increases with the amount of water till one molecule of water is present for one molecule of acid (1.0754), *i.e.*, until the hydrate, $C_2H_4O_2 . H_2O$, or $CH_3{-}C(OH)_3$, *ortho-acetic acid* is formed.

The amount of acetic acid in a vinegar is therefore estimated by exactly neutralizing a measured portion of the acid with a dilute solution of soda, the amount of sodium hydroxide in which is known. This is called *volumetric analysis*, or *titration*.

The following acetates are worthy of attention :

Potassium acetate, $C_2H_3O_2K$, is made by dissolving potassium hydroxide or carbonate in acetic acid. It is a white deliquescent powder. Its solution in concentrated acetic acid separates on evaporation the acid salt, $C_2H_3O_2K + C_2H_4O_2$, in mother-of-pearl leaflets, which fuse at 148°, and at 200° are resolved into the neutral salt and acetic acid.

Sodium acetate, $C_2H_3O_2Na$. It is made by neutralizing acetic acid with sodium hydroxide or carbonate. It crystallizes in prisms containing three molecules of water, and is efflorescent. At 77° it fuses, losing its water of crystallization and becoming solid again. The anhydrous sodium acetate fuses at 319°.

Zinc acetate, $(C_2H_3O_2)_2Zn$, is obtained by dissolving zinc carbonate in acetic acid. It forms large, colorless, rhombic crystals, which have a fatty feel. They smell of acetic acid and are easily soluble in water.

Plumbic acetate, sugar of lead, $(C_2H_3O_2)_2Pb, 3H_2O$, is made by dissolving lead oxide in dilute acetic acid. It is a beautifully crystalline compound, which is soluble in 1½ parts of water. It has a sweet taste, with a disagreeable metallic after-taste. It fuses at 75°, at 100° loses its

water of crystallization, and becomes solid, fusing again at 280°. It is a powerful poison. A solution of plumbic acetate dissolves two molecules of plumbous oxide, forming $(C_2H_3O_2)_2Pb + 2\ PbO$, *basic lead acetate*, which is also soluble in water.

Cupric acetate, distilled verdigris, $(C_2H_3O_2)Cu$, is obtained by dissolving copper in acetic acid. Dark green prisms with a nauseous taste. Easily soluble in water. The ordinary verdigris corresponds to the basic lead acetate.

Silver acetate, $C_2H_3O_2Ag$, precipitates as a white compound when silver nitrate and sodium acetate solutions are brought together. It is difficultly soluble in cold water, more easily in hot water, from which it crystallizes in long flexible needles.

Ethyl Acetic Ester, Acetic Ether, Ethyl Acetate, $CH_3{}^-COO^-C_2H_5$, or $C_4H_8O_2$.

A mixture of 3.6 parts of alcohol and 9 parts of sulphuric acid is poured over 6 parts of sodium acetate, and, after standing, distilled.

Acetic ester is a colorless liquid with a refreshing odor, boiling at 77°. It is easily combustible, and is miscible with alcohol and ether, and is soluble in 11 parts of water. It has a burning taste. It gradually decomposes in contact with water into alcohol and acetic acid.

Characteristics of the Esters of the Organic Acids.

This class of compounds is formed either by the direct action of the acid on the alcohol, or by the action of a salt of the acid on the chloride, bromide, or iodide of a hydrocarbon (alkylogen) :

$$C_2H_5Br + \underset{\text{Sodium acetate}}{CH_3{}^-COONa} = CH_3{}^-COOC_2H_5 + NaBr,$$

or by the action of an acid sulphuric ester on a salt of the organic acid.

$$\underset{\text{Ethylsulphuric acid}}{\begin{matrix}C_2H_5O\\HO\end{matrix}\!\!>\!SO_2} + CH_3COONa = CH_3COOC_2H_5 + \begin{matrix}NaO\\HO\end{matrix}\!\!>\!SO_2$$

It is, however, not usually necessary to produce the acid sulphuric ester in the pure state. The alcohol is mixed with the sulphuric acid and the salt of the organic acid, and the whole distilled. The esters can also be produced by saturating a mixture of the alcohol and the organic acid with chlorhydric acid gas. In this case the chlorhydric acid acts most probably as a dehydrating agent:

$$\underset{\text{Acetic acid}}{C_2H_4O_2} + \underset{\text{Alcohol}}{C_2H_6O} = \underset{\text{Acetic ester}}{C_2H_3O_2{}^-C_2H_5} + H_2O.$$

The esters are decomposed into the alcohol and a salt of the acid by boiling with an alkali :

$$\underset{\text{Acetic ester}}{CH_3{}^-COO{}^-C_2H_5} + NaOH = \underset{\text{Sodium acetate}}{CH_3{}^-COONa} + \underset{\text{Alcohol}}{C_2H_5OH}.$$

The ease with which a halogen substitution of a hydrocarbon and a salt of an organic acid yield the ester, and the facility with which the ester thus formed yields the alcohol by boiling with an alkali, affords us a most excellent method for producing alcohols from chlorides, bromides, etc.

$$\underset{\text{Ethyl chloride}}{CH_3{}^-CH_2Cl} + \underset{\text{Sodium acetate}}{CH_3{}^-COONa} = \underset{\text{Acetic ethyl ester}}{CH_3{}^-COO{}^-CH_2{}^-CH_3} + NaCl$$

$$\underset{\text{Acetic ethyl ester}}{CH_3{}^-COO{}^-CH_2{}^-CH_3} + KOH = \underset{\text{Potassium acetate}}{CH_3{}^-COOK} + \underset{\text{Alcohol}}{CH_3{}^-CH_2OH}.$$

With ammonia, the esters yield acid amides and alcohol :

$$CH_3{}^-COOC_2H_5 + NH_3 = CH_3{}^-CONH_2 + C_2H_5OH.$$

Metallic sodium acts on acetic ester substitutingly, liberating hydrogen and forming, besides sodium ethoxide, the sodium compound of a complicated compound ether, *acetoacetic ester:*

$$2\,CH_3{}^-COOC_2H_5 + Na_2 = H_2 + C_2H_5ONa + CH_3{}^-CO{}^-CHNa{}^-COOC_2H_5.$$

In this compound, the sodium atom can be replaced by both alcohol and acid rests.

The sodium aceto-acetic ester is easily decomposed by acids, yielding the *aceto-acetic ester*, $C_6H_{10}O_3 = CH_3{-}CO{-}CH_2{-}COOC_2H_5$, a colorless liquid boiling at 181°, which by the action of sodium is converted back into the sodium aceto-acetic ester. As the sodium atom can be replaced by means of the chlorides, bromides, and iodides of both alcohol and acid rests, and the compounds thus formed can be decomposed in a characteristic manner by potash, the aceto-acetic ester is used as the starting-out point for the production of a great number of compounds.

By the action of ethyl iodide on sodium aceto-acetic ester, *ethyl-aceto-acetic* ester is formed, $C_8H_{14}O_3 = CH_3{-}CO{-}CH(C_2H_5){-}CO_2C_2H_5$, which by the action of sodium yields, with evolution of hydrogen, *sodium ethyl-aceto-acetic ester*. This by treatment with ethyl iodide yields *di-ethyl-aceto-acetic ester*, $C_{10}H_{18}O_3 = CH_3{-}CO{-}C(C_2H_5)_2{-}CO_2C_2H_5$. Acetyl chloride and other aci-chlorides give with sodium aceto-acetic ester the corresponding aci-compounds, viz., $CH_3{-}CO{-}CH(C_2H_3O){-}CO_2C_2H_5$.

The decomposition of aceto-acetic ester and its derivatives takes place in two ways. (1) Out of each molecule, two acids are formed, one of which is always acetic acid :

1) $\underset{\text{Aceto-acetic-ester}}{CH_3{-}CO{-}CH_2{-}CO_2C_2H_5} + 2\ H_2O = \underset{\text{Acetic acid}}{CH_3{-}CO_2H} + \underset{\text{Acetic acid}}{CH_3{-}CO_2H} + C_2H_6O.$

2) $\underset{\text{Ethylaceto-acetic ester}}{CH_3{-}CO{-}CH(C_2H_5){-}CO_2C_2H_5} + 2\ H_2O = \underset{\text{Acetic acid}}{CH_3{-}CO_2H} + \underset{\text{Butyric acid}}{CH_2(C_2H_5){-}CO_2H} + C_2H_6O.$

3) $\underset{\text{Di-ethyl-aceto-acetic ester}}{CH_3{-}CO{-}C(C_2H_5)_2{-}CO_2C_2H_5} + 2\ H_2O = \underset{\text{Acetic acid}}{CH_3{-}CO_2H} + \underset{\text{Di-ethylacetic acid}}{CH(C_2H_5)_2{-}CO_2H} + C_2H_6O.$

(2) Carbonic acid and a ketone are formed :

1) $\underset{\text{Aceto-acetic ester}}{CH_3{-}CO{-}CH_2{-}CO_2C_2H_5} + H_2O = \underset{\text{Acetone}}{CH_3{-}CO{-}CH_3} + CO_2 + C_2H_6O.$

2) $\underset{\text{Ethylaceto-acetic ester}}{CH_3{-}CO{-}CH(C_2H_5){-}CO_2C_2H_5} + H_2O = \underset{\text{Methylpropylketone}}{CH_3{-}CO{-}CH_2(C_2H_5)} + CO_2 + C_2H_6O.$

3) $\underset{\text{Diethylaceto-acetic ester}}{CH_3{-}CO{-}C(C_2H_5)_2{-}CO_2C_2H_5} + H_2O = \underset{\text{Methylamylketone}}{CH_3{-}CO{-}CH(C_2H_5)_2} + CO_2 + C_2H_6O.$

In both cases the ester is saponified with the formation of alcohol. The esters homologous with acetic ester behave in the same manner.

Acetic acid when treated with phosphorus trichloride exchanges its OH for Cl, forming

Acetyl Chloride, $CH_3{}^-CO^-Cl$, or C_2H_3OCl :

$$3\,CH_3{}^-COOH + PCl_3 = 3\,CH_3{}^-COCl + PH_3O_3.$$

It is a colorless very mobile liquid with a penetrating odor. It boils at 55°, and fumes slightly in the air.

Acetyl chloride is our first example of an aci-chloride. Aci-chlorides exchange their chlorine very easily for other elements or atomic groups. They are all decomposed by water with regeneration of the acid :

$$CH_2COCl + HHO = CH_3COOH + HCl.$$

Even the moisture of the air decomposes them gradually. With an alcohol, the ester is formed :

$$CH_3{}^-COCl + CH_3OH = \underset{\text{Methyl acetic ester}}{CH_3{}^-CO^-OCH_3} + HCl.$$

With ammonia, the amide :

$$CH_3COCl + 2\,NH_3 = CH_3{}^-CONH_2 + NH_4Cl.$$

With salts of the organic acids, the anhydride :

$$CH_3{}^-COCl + CH_3{}^-COONa = \underset{\text{Acetic anhydride}}{CH_3{}^-CO^-O^-CO^-CH_3} + NaCl.$$

In a similar manner the acetyl bromide and acetyl iodide have been produced. Both are liquids, the former boiling at 81°, the latter at 108°. By action of silver cyanide, $CH_3{}^-CO^-CN$, on acetyl chloride, *acetyl cyanide* is formed. It is a liquid boiling at 93°, and by the action of chlorhydric acid is converted into pyroracemic acid.

Acetamide, $CH_3{}^-CO^-NH_2$, is obtained by the action of ammonia on acetic ester, and by the distillation of ammonium acetate :

$$CH_3{}^-COO(NH_4) = CH_3{}^-CO(NH_2) + H_2O.$$

Acetamide is also produced by heating acetic acid with potassium sulphocyanide for several days. At first, potassium acetate and sulphocyanic acid are formed. The latter then acts on the free acetic acid:

$$CH_3{-}COOH + HSCN = \underset{\text{Acetamide}}{CH_3{-}CO{-}NH_2} + \underset{\substack{\text{Carbon}\\\text{oxysulphide}}}{COS}.$$

Acetamide is a colorless, crystalline substance fusing at 78°, and boiling at 222°. It has a peculiar odor. Phosphoric anhydride acts dehydratingly on it, forming acetonitrile (methyl cyanide):

$$CH_3{-}CO{-}NH_2 - H_2O = CH_3{-}CN.$$

By heating acetic acid with acetonitrile, *diacetamide*, $\begin{matrix}CH_3{-}CO\\CH_3{-}CO\\H\end{matrix}\!\!>\!\!N$, is formed, which is very similar to acetamide:

$$CH_3{-}CN + CH_3{-}COOH = \begin{matrix}CH_3{-}CO\\CH_3{-}CO\\H\end{matrix}\!\!>\!\!N.$$

It fuses at 59° and boils at 210°–215°.

By heating acetic anhydride (see below) with acetonitrile, *triacetamide*, $\begin{matrix}CH_3{-}CO\\CH_3{-}CO\\CH_3{-}CO\end{matrix}\!\!>\!\!N$, is formed, which also resembles acetamide. It fuses at 78°.

$$CH_3{-}CN + \begin{matrix}CH_3{-}CO\\CH_3{-}CO\end{matrix}\!\!>\!\!O = \begin{matrix}CH_3{-}CO\\CH_3{-}CO\\CH_3{-}CO\end{matrix}\!\!>\!\!N.$$

When acetyl chloride and sodium acetate are distilled together, there is formed, besides sodium chloride,

Acetic Anhydride, $\begin{matrix}CH_3{-}CO\\CH_3{-}CO\end{matrix}\!\!>\!\!O$. A colorless liquid with an odor resembling acetic acid. It boils at 138°. It sinks in water, and is gradually decomposed by it into acetic acid:

$$\begin{matrix}CH_3{-}CO\\CH_3{-}CO\end{matrix}\!\!>\!\!O + H_2O = 2\,CH_3{-}COOH.$$

Barium peroxide converts acetic anhydride into *acetyl superoxide*, $\begin{matrix}CH_3{-}CO{-}O\\CH_3{-}CO{-}O\end{matrix}$, or $C_4H_6O_4$. It is a thick oil, which acts as a strong oxidizing agent, and, when heated, explodes.

By leading chlorine into acetic acid, the hydrogen of the methyl is replaced by chlorine, and the following compounds are obtained :

1) *Monochloracetic acid*, CH_2Cl^-COOH, a crystalline, deliquescent mass. It fuses at 62° and boils at 187°. It forms crystalline salts, and exchanges its chlorine atom for other mono-valent atomic groups.

2) *Dichloracetic acid*, $CHCl_2^-COOH$, is an easily fusible, crystalline substance boiling at 195°. Its *ethyl ester*, $CHCl_2^-COOC_2H_5$, is formed by the action of potassium cyanide on an alcoholic solution of chloral hydrate. It is a liquid boiling at 156°.

3) *Trichloracetic acid*, CCl_3^-COOH, is also obtained by the oxidation of chloral. It is a crystalline, deliquescent substance, boiling at 200°. Potassium hydroxide decomposes it into chloroform and potassium carbonate :

$$CCl_3^-COOH + 2\,KOH = CCl_3H + K_2CO_3 + H_2O.$$

By the action of sulphuric anhydride, acetic acid is converted into *acetosulphonic acid*, $CH_2(SO_3H)^-COOH$, a crystalline, easily soluble, dibasic acid.

As yet we have considered only those oxygen derivatives of ethane in which the hydrogen atoms of the second CH_3 remained intact, or, at most, were replaced by chlorine atoms. If, however, the hydrogen atoms of the second CH_3 are replaced by hydroxyls, compounds are formed which are alcohols, aldehydes, or acids, depending on the number of H's replaced by hydroxyl.

If one H in each of the CH_3-groups is replaced by an OH, the compound, $CH_2(OH)^-CH_2(OH)$, is formed. This naturally possesses alcoholic properties, as it is, in fact, a double alcohol. Similar compounds are also known in the C_3, C_4, and C_5 series. They are called *Glycols*.

The H of the hydroxyl groups can be replaced by hydrocarbon rests, ethylene glycol, $\begin{matrix} CH_2^-OH \\ | \\ CH_2^-OH \end{matrix}$, yielding the mono-ethyl ether and di-ethyl ether :

$$\begin{matrix} CH_2(OC_2H_5) \\ | \\ CH_2(OH) \end{matrix} \quad \text{and} \quad \begin{matrix} CH_2(OC_2H_5) \\ | \\ CH_2(OC_2H_5) \end{matrix}.$$

The mono-acetyl, di-acetyl, and nitric esters are also known :

$$\begin{array}{lll} CH_2(O\text{-}C_2H_3O) & CH_2(OC_2H_3O) & CH_2(ONO)_2 \\ | & | & | \\ CH_2(OH) & CH_2(OC_2H_3O) & CH_2(ONO)_2 \end{array}$$

Ethylene Glycol, Ethylene Alcohol, $CH_2(OH)\text{-}CH_2(OH)$, or $C_2H_6O_2$, contains one more O than ethyl alcohol. It is made from ethylene bromide :

By digesting ethylene iodide with silver acetate, the di-acetyl glycol ester is obtained:

$$CH_2I\text{-}CH_2I + 2\,AgC_2H_3O_2 = \begin{matrix} CH_2(C_2H_3O_2) \\ | \\ CH_2(C_2H_3O_2) \end{matrix} + 2\,AgI,$$

which, by boiling with potassium hydroxide, is converted into glycol :

$$\begin{matrix} CH_2(C_2H_3O_2) \\ | \\ CH_2(C_2H_3O_2) \\ \text{Ethylene acetate} \end{matrix} + \begin{matrix} KHO \\ KHO \end{matrix} = \begin{matrix} CH_2(OH) \\ | \\ CH_2(OH) \\ \text{Glycol} \end{matrix} + \begin{matrix} C_2H_3O_2K \\ C_2H_3O_2K \\ \text{Potassium acetate} \end{matrix}$$

It is a colorless, odorless, viscous liquid, boiling at 197°. On digestion with chlorhydric acid, it is converted into $CH_2Cl\text{-}CH_2(OH)$, *glycol-chlorhydrin,* which by treatment with potassium hydroxide is decomposed into *ethylene oxide:*

$$\begin{matrix} CH_2\text{-}CH_2 \\ \diagdown\ \diagup \\ O \end{matrix}$$

$$CH_2Cl\text{-}CH_2OH + KOH = \underset{\substack{\text{Ethylene} \\ \text{oxide}}}{C_2H_4O} + KCl + H_2O.$$

Polyglycols are formed with glycol. They are constituted as follows :

Di-ethylene glycol,

$$C_4H_{10}O_3 = CH_2(OH)\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2(OH).$$

Tri-ethylene glycol, $C_6H_{14}O_4$

$$= CH_2(OH)\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2(OH), \text{ etc.}$$

These glycols stand in the same relation to glycol as ordinary ether to alcohol.

As acetic acid is derived from alcohol, *glycollic acid*, $CH_2OH^{-}COOH$, is derived from glycol. It is produced by boiling monochloracetic acid with an alkali :

$$CH_2Cl^{-}COOH + KOH = CH_2(OH)^{-}COOH + KCl.$$

It can also be obtained by oxidizing glycol in the same manner that acetic acid is formed from alcohol.

We see from the formula of glycollic acid that it must combine the properties of an alcohol and an acid. If the H of the carboxyl group be replaced by the ethyl group, $CH_2(OH)^{-}COOC_2H_5$ is formed, which is the ester of glycollic acid and analogous to acetic ester. If the H of the hydroxyl, however, is replaced by the same group, $CH_2(OC_2H_5)^{-}COOH$ is obtained, which is a new acid, *ethoxyglycollic acid*, and which neutralizes bases with the same power as glycollic acid. If the hydroxyl of glycollic acid be replaced by the amido-group, NH_2, a neutral body, $CH_2(OH)^{-}CONH_2$, *glycol-amide*, analogous to acetamide, is formed. The introduction of NH_2 in place of the OH of the CH_2OH, influences the compound but little, and the compound which is obtained, $CH_2(NH_2)COOH$, *amido-acetic acid*, or *glycocoll*, is a decided acid. We see hence that there are a great number of isomeric compounds depending on which carbon atom is involved in the substitution. The more important will be mentioned.

Glycollic acid is a white, deliquescent, crystalline mass, fusing at 80°. It cannot be distilled without decomposition. In water and alcohol it is very soluble. It forms salts, esters, and ester acids. Phosphorus trichloride converts it into *glycollic chloride:*

$$3\,CH_2(OH)^{-}COOH + 2\,PCl_3 = 3\,CH_2Cl^{-}COCl + 2\,PH_3O_3,$$

which is identical with monochloracetyl chloride. It is decomposed by water into monochloracetic acid and chlorhydric acid :

$$CH_2Cl^{-}COCl + H_2O = CH_2Cl^{-}COOH + HCl.$$

Of the other substitutions of glycollic acid we shall mention only *glycolamide*, $CH_2(OH)^-CO(NH_2)$, which forms colorless crystals easily soluble in water, and slightly in alcohol; and

Glycocoll, Amido-acetic acid, Glycine, $CH_2(NH_2)^-COOH$, which is formed by the decomposition of glue by sulphuric acid, and from many substances existing in the animal organism (bile acids, uric acid, hippuric acid). It is also formed by the action of monobromacetic acid on ammonia:

$$CH_2Br^-COOH + NH_3 = CH_2(NH_2)^-COOH + HBr.$$

Large, colorless, rhombohedral crystals, fusing at 170°. It is stable in the air, easily soluble in water, and insoluble in alcohol.

Glycocoll is a weak acid, exchanging the H of its hydroxyl for bases. It also combines with acids, since it is both an amine-base as well as an acid. The *copper compound*, $(C_2H_4NO_2)_2Cu + H_2O$, which is obtained by dissolving copper oxide in a hot solution of glycocoll, is a characteristic example of this class of salts. It crystallizes in deep blue needles.

In the same manner that glycol forms poly-glycols, glycollic acid yields *poly-glycollic acids*. *Di-glycollic acid*, $C_4H_6O_5 = CO_2H^-CH_2^-O^-CH_2^-CO_2H$, which is formed with glycollic acid, when the latter is made from mono-chloracetic acid, is an example of this class.

Glycollic acid forms a peculiar anhydride, glycollide:

$$C_4H_4O_4, O\begin{matrix}\diagup CO^-CH_2\diagdown \\ \diagdown CH_2^-CO\diagup\end{matrix}O.$$

It is an amorphous powder, which by boiling with alkalis or water is converted back into glycollic acid.

Besides ordinary aldehyde, there are two other bodies of an aldehyde nature derived from ethane, viz., *glyoxal*, CHO^-CHO, and *glyoxalic acid*, CHO^-COOH. Finally, by complete hydroxylation of all the hydrogen of ethane, we derive—

Oxalic Acid, $COOH^-COOH$, or $C_2H_2O_4$. Oxalic acid is a di-basic acid, as it contains two carboxyl groups.

Oxalic acid is largely distributed in the vegetable kingdom in the form of potassium, sodium, and calcium salts. It is formed by the oxidation of many carbon compounds, particularly the fats and carbhydrates (sugar, starch, gum, wood-fibre, etc.). It is made commercially by heating saw-dust with potassium or sodium hydroxide.

It crystallizes in large, transparent, colorless prisms, containing two molecules of water, which it loses at 100°. It is easily soluble in water and alcohol. It is poisonous. By careful heating it sublimes at 150°. When heated rapidly, it decomposes into carbonic acid, carbonous oxide, and water. It suffers the same decomposition on heating with concentrated sulphuric acid. When heated with glycerol, it breaks into carbonic acid and formic acid :

$$C_2H_2O_4 = CO_2 + CO + H_2O.$$
$$C_2H_2O_4 = CO_2 + CH_2O_2.$$

Oxalic acid acts as a reducing agent. It precipitates gold and platinum from their chlorides, and is oxidized itself into carbonic acid :

$$PtCl_4 + 2\,C_2H_2O_4 = Pt + 4\,CO_2 + 4\,HCl.$$

In the same manner it reduces manganese di-oxide to manganous salts, decolorizes potassium permanganate, etc.

Oxalic acid forms two series of salts, viz., acid, in which one H, and neutral, in which both H's are replaced by metals. Double salts of it are also known.

The following are of importance. *Potassium hydrogen oxalate, binoxalate of potash*, KHC_2O_4, slightly soluble in cold water. *Ammonium hydrogen oxalate*, $(NH_4)HC_2O_4$; on heating, water splits out and *oxamic acid*, $COOH^{-}CO(NH_2)$, is formed. *Ammonium oxalate* $(NH_4)_2C_2O_4$; on heating, it gives *oxamide*, $CO(NH_2)^{-}CO(NH_2)$. *Calcium oxalate*, CaC_2O_4, completely insoluble in water. Its formation is used as a test for oxalic acid as well as for its separation. The oxalates of silver and mercury decompose, on heating, with explosion, and break into carbonic acid and the metal.

Oxalic acid forms two series of esters:

Methyl-oxalic acid, $\begin{matrix}COOH\\ |\\ COOCH_3\end{matrix}$, and

Oxalic methyl ester, $\begin{matrix}COOCH_3\\ |\\ COOCH_3\end{matrix}$, monoclinic tablets fusing at 51° and boiling at 162°. It is used for the production of pure methyl alcohol.

Ethyl-oxalic acid, $\begin{matrix}COOH\\ |\\ COOC_2H_5\end{matrix}$, and

Oxalic ethyl ester, $\begin{matrix}COOC_2H_5\\ |\\ COOC_2H_5\end{matrix}$, liquid boiling at 186°. Water decomposes it gradually into oxalic acid and alcohol.

Oxalic acid forms also two amido-substitutions:

Oxamic acid, $\begin{matrix}COOH\\ |\\ CO(NH)_2\end{matrix}$, which is obtained by heating ammonium hydrogen oxalate:

$$\begin{matrix}COOH\\ |\\ COO(NH_4)\end{matrix} - H_2O = \begin{matrix}COOH\\ |\\ CO(NH_2)\end{matrix};$$

or by boiling oxamide with aqueous ammonia, the ammonium salt of oxamic acid being formed:

$$\begin{matrix}CO(NH_2)\\ |\\ CO(NH_2)\end{matrix} + H_2O = \begin{matrix}COO(NH_4)\\ |\\ CO(NH_2)\end{matrix}.$$

Oxamic acid is a white, crystalline powder.

Oxamide, $\begin{matrix}CO(NH_2)\\ |\\ CO(NH_2)\end{matrix}$, is produced by the distillation of neutral ammonium oxalate:

$$\begin{matrix}COO(NH_4)\\ |\\ COO(NH_4)\end{matrix} - 2\,H_2O = \begin{matrix}CO(NH_2)\\ |\\ CO(NH_2)\end{matrix};$$

or by the action of aqueous ammonia on oxalic ethyl ester:

$$\begin{matrix}COO(C_2H_5)\\ |\\ COO(C_2H_5)\end{matrix} + 2\,NH_3 = \begin{matrix}CO(NH_2)\\ |\\ CO(NH_2)\end{matrix} + 2\,C_2H_6O.$$

It is a white powder almost insoluble in water. When heated with phosphoric anhydride, it yields cyanogen:

$$\begin{matrix}CO(NH_2)\\ |\\ CO(NH_2)\end{matrix} = C_2N_2 + 2\,H_2O.$$

Phosphoric anhydride acts as a dehydrating agent, because it has a strong tendency to pass into phosphoric acid.

Cyanogen may be considered as the nitrile of oxalic acid in the same way that cyanhydric acid is the nitrile of formic acid, and methyl cyanide the nitrile of acetic acid. All nitriles are converted into their corresponding acids by the addition of the elements of water :

$$\underset{\text{Cyanhydric acid}}{HCN} + 2\,H_2O = \underset{\text{Formic acid}}{HCO_2H} + NH_3$$

$$\underset{\text{Methyl cyanide}}{CH_3{-}CN} + 2\,H_2O = \underset{\text{Acetic acid}}{CH_3{-}CO_2H} + NH_3$$

$$\underset{\text{Cyanogen}}{\begin{matrix}CN\\ |\\ CN\end{matrix}} + 4\,H_2O + \underset{\text{Oxalic acid}}{\begin{matrix}CO_2H\\ |\\ CO_2H\end{matrix}} + 2\,NH_3.$$

Since oxalic ethyl ester yields oxamide when treated with ammonia, it gives substituted oxamides when treated with substituted amines. With ethylamine, for example, *di-ethyloxamide* is produced.

Phosphorus pentachloride converts oxamide into a very unstable compound, $\begin{matrix}CCl_2{-}NH_2\\ |\\ CCl_2{-}NH_2\end{matrix}$, from which HCl is eliminated, forming first $\begin{matrix}CCl{=}NH\\ |\\ CCl{=}NH\end{matrix}$, and then $\begin{matrix}C{\equiv}N\\ |\\ C{\equiv}N\end{matrix}$. If dimethyloxamide or diethyloxamide, $\begin{matrix}CO{-}NHCH_3\\ |\\ CO{-}NHCH_3\end{matrix}$, is taken instead of oxamide, the chlorine compound which is formed loses three molecules of HCl, forming the bases *chloroxalmethyline*, $C_4H_3ClN_2$, and *chloroxalethyline*, $C_6H_9ClN_2$.

Sulpho-Substitutions of Ethane.

The sulpho-substitutions of ethane are not as numerous as the oxygen derivatives, and on account of their lesser importance only a few of the better known will be mentioned.

Ethylmercaptan, $CH_3{-}CH_2{-}SH$, or C_2H_6S, corresponds to the ethyl alcohol. It is produced by the distillation of potassium ethylsulphate or ethyl chloride with potassium sulphydrate :

$$C_2H_5(KSO_4) + KSH = C_2H_5(SH) + K_2SO_4$$
$$C_2H_5(Cl) + KSH = C_2H_5(SH) + KCl.$$

It is a colorless liquid with a highly offensive odor. It boils at 36°, is but slightly soluble in water, and is miscible with alcohol and ether. The H of its SH is easily replaced by metals, forming mercaptides (C_2H_5SK). Fuming nitric acid oxidizes it into ethylsulphonic acid :

$$C_2H_5SH + O_3 = C_2H_5{-}SO_3H.$$

By distilling potassium ethylsulphate with potassium sulphide we obtain :

Ethyl Sulphide, $\begin{matrix}CH_3{-}CH_2\\CH_3{-}CH_2\end{matrix}\!\!>\!S$, corresponding to ether. Colorless liquid with the odor of garlic, boiling at 91°. Fuming nitric acid oxidizes it to *di-ethyl-sulphone,* $(C_2H_5)_2SO_2$.

The oxidation of mercaptan to sulphonic acid, and of the sulphide to sulphone, is exactly analogous to the oxidation of the phosphines to phosphinic acids (vid. p. 68). Hydrogen sulphide is oxidized to sulphuric acid, the sulphur taking up two atoms of oxygen and both the H's being converted into hydroxyls :

$$\begin{matrix}H\\H\end{matrix}\!\!>\!S \text{ passes into } \begin{matrix}HO\\HO\end{matrix}\!\!>\!SO_2.$$

The same reaction takes place when the hydrogen is replaced by organic atomic groups, with the exception that the oxidation does not extend to the latter :

$$\begin{matrix}C_2H_5\\H\end{matrix}\!\!>\!S \text{ yields } \underset{\text{Ethylsulphonic acid}}{\begin{matrix}C_2H_5\\HO\end{matrix}\!\!>\!SO_2}$$

$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>\!S \text{ yields } \underset{\text{Diethylsulphone}}{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>\!SO_2.}$$

In these compounds the sulphur is of course hexa-valent as in sulphuric acid.

Ethyl sulphide unites directly with ethyl iodide :

$$(C_2H_5)_2S + C_2H_5I = (C_2H_5)_3SI.$$

The constitution of this compound is $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>\!S\!<\!\begin{matrix}C_2H_5\\I\end{matrix}$.

The atom of iodine can be replaced by any acid rest or by hydroxyl. In the latter case, a strongly basic substance is formed, which attracts carbonic acid from the air. These peculiar compounds, which show sulphur to be a tetra-valent element occur in the other carbon series, and are called *sulphine compounds.* This one in particular is *tri-ethyl-sulphine iodide.*

If potassium ethylsulphate is distilled with K_2S_2, instead of K_2S, we obtain :

Ethyl Disulphide, $\begin{matrix} CH_3{}^-CH_2{}^-S \\ CH_3{}^-CH_2{}^-S \end{matrix}$, or $C_4H_{10}S_2$, to which there is no corresponding oxygen compound. It is similar to ethyl sulphide in its properties and boils at 151°.

Ethyl Sulphaldehyde, $CH_3{}^-CHS$, or C_2H_4S, corresponds to ethyl aldehyde. It is obtained by leading hydrogen sulphide through aldehyde. An oil is formed which is decomposed by acids, yielding sulphaldehyde, a white, crystalline body. It is properly the triple polymer $3\ C_2H_4S = C_6H_{12}S_3$. The simple aldehyde has not yet been obtained.

Thiacetic acid, $CH_3{}^-COSH$, or C_2H_4SO, corresponding to acetic acid. It is formed by the action of phosphorus pentasulphide on acetic acid, or acetyl chloride on potassium sulphydrate :

$$5\ CH_3{}^-COOH + P_2S_5 = 5\ CH_3{}^-COSH + P_2O_5$$
$$CH_3{}^-COCl + KHS = CH_3{}^-COSH + KCl.$$

Colorless liquid with the odor of both acetic acid and hydrogen sulphide. It boils at 93°, and forms salts and esters.

Thiacetic anhydride, $\begin{matrix} CH_3{}^-CO \\ CH_3{}^-CO \end{matrix}\!\!>\!S$, is formed by the action of P_2S_5 on acetic anhydride. It is a colorless liquid boiling at 121°.

By the action of ethyl iodide on sodium or ammonium sulphite, *ethyl-sulphonic acid,* $C_2H_5{}^-SO_3H$, is formed. Its salts are well known. It is identical with the acid obtained by the oxidation of ethyl mercaptan.

Nitrogen Substitutions of Ethane.

Ethylamine, $C_2H_5{}^-NH_2$, or C_2H_7N, is made from ethyl iodide and ammonia, or from ethyl cyanic ether and potassium hydroxide. It is a colorless liquid with an ammoniacal odor, boiling at 18°. It yields crystalline salts with acids.

Di-ethylamine, $(C_2H_5)_2NH$, or $C_4H_{11}N$, is made from ethyl iodide and ammonia. It boils at 57°.

Tri-ethylamine, $(C_2H_5)_3N$, or $C_6H_{15}N$, is made in the same manner. It boils at 96°.

Tetra-ethylammonium iodide, $(C_2H_5)_4NI$, is the final product of the reaction of ammonia on ethyl iodide. It is a white, crystalline mass. With silver iodide it yields:

Tetra-ethylammonium hydroxide, $(C_2H_5)_4N^-OH$, which is a base resembling potassium hydroxide.

By the action of ammonia on ethylene chloride, $CH_2Cl^-CH_2Cl$, analogous compounds are formed:

Ethylene-diamine, $\begin{matrix}CH_2{}^-NH_2\\ |\\ CH_2{}^-NH_2\end{matrix}$, or $C_2H_4(NH_2)_2$.

Di-ethylene-diamine, $\begin{matrix}C_2H_4\\ C_2H_4\end{matrix}\!\!>\!(NH)_2$.

Tri-ethylene-diamine, $\begin{matrix}C_2H_4\\ C_2H_4\\ C_2H_4\end{matrix}\!\!>\!N_2$.

They are liquids of basic character.

Glycolchlorhydrin unites with ammonia and amine bases, particularly with the tertiary amines, forming substituted ammonium compounds. The compound with trimethylamine is $\begin{matrix}CH_2{}^-OH\\ |\\ CH_2{}^-N(CH_3)_3Cl\end{matrix}$, *trimethyloxethyl-ammonium chloride*. The *hydroxide*, $\begin{matrix}CH_2{}^-OH\\ |\\ CH_2{}^-N(CH_3)_3OH\end{matrix}$, exists in the bile. It can be produced by the action of alkalis on a substance occurring in white mustard seeds (sinapin), and is called *choline*. It is a strongly basic body, and gives with iodohydric acid the compound $\begin{matrix}CH_2{}^-I\\ |\\ CH_2{}^-N(CH_3)_3I\end{matrix}$, *tri-*

methyliodoëthylammonium iodide. This iodide when treated with moist silver oxide yields the oxide $\begin{matrix}CH_2{}^-O\\ |\quad\quad |\\ CH_2{}^-N\Xi(CH_3)_3\end{matrix}$, which is contained in the substance of the brain, and is called *neurine*. By the oxidation of neurine or choline, *oxyneurine*, $\begin{matrix}CO\ {}^-O\\ |\quad\quad |\\ CH_2{}^-N(CH_3)_3\end{matrix}$, is obtained. It exists in the sugar beet (beta vulgaris), and is called *betaïne*. It is formed by heating monochloracetic acid with trimethylamine.

By the action of silver nitrite on ethyl iodide, *Nitro-ethane*, $C_2H_5{}^-NO_2$, is formed (isomeric with ethyl nitrous ester). It is a liquid boiling at 112°.

The only other compounds of the C_2 series which we shall mention are the following. Their methods of preparation will be found under the corresponding substances of the C_1 series.

Ethylphosphine, $C_2H_5PH_2$, boils at 25°.

Di-ethylphosphine, $(C_2H_5)_2PH$, boils at 85°.

Tri-ethylphosphine, $(C_2H_5)_3P$, boils at 127°.

They are all obtained according to the methods given under the corresponding compounds in the methane series. They are easily oxidized, the ethylphosphine to *ethylphosphinic acid*, $C_2H_5PO(OH)_2$, di-ethylphosphine to *di-ethylphosphinic acid*, $(C_2H_5)_2PO(OH)$, tri-ethylphosphine to *tri-ethylphosphinic oxide* $(C_2H_5)_3PO$.

Tri-ethylarsine, $(C_2H_5)_3As$, boils at 140°, fumes in the air, and on warming in the air takes fire.

Tri-ethylstibine, $(C_2H_5)_3Sb$, boils at 158°, fumes in the air, and takes fire.

Zinc-ethyl, $(C_2H_5)_2Zn$, boils at 118°, and takes fire at once when exposed to the air.

Mercury-ethyl, $(C_2H_5)_2Hg$, boils at 159°. It is extremely poisonous.

These compounds are all obtained by reactions analogous to those of the corresponding methyl compounds.

The following esters are worthy of notice.

Ethyl cyanide, $C_2H_5{}^-CN$, is produced from potassium ethylsulphate and potassium cyanide. It is a liquid with an ethereal odor, boiling at 98°. On boiling with alkalis, it is decomposed into ammonia and propionic acid. It is therefore the stepping-stone from the C_2 to the C_3 series :

$$C_2H_5{}^-CN + 2\ H_2O = \underset{\text{Propionic acid}}{C_2H_5{}^-COOH} + NH_3.$$

It is hence *propionitrile.*

Ethyl isocyanide is prepared from silver cyanide and ethyl iodide. It is a liquid with an offensive bitter odor, and boils at 79°. Acids decompose it at once into ethylamine and formic acid :

$$C_2H_5{}^-NC + 2\ H_2O = C_2H_5(NH_2) + CH_2O_2.$$

Ethyl-cyanic ether, $CON^-C_2H_5$, is obtained by the dry distillation of potassium cyanate with potassium ethylsulphate. It is a colorless liquid with a strong odor which irritates the eyes. It boils at 60°. With it there is formed

Ethyl-cyanuric ether, $C_3O_3N_3 . (C_2H_5)_3$, which forms large crystals fusing at 85° and boiling at 276°. Potassium hydroxide decomposes both the cyanic and cyanuric ether into ethylamine and potassium carbonate :

$$CON^-C_2H_5 + 2\ KHO = K_2CO_3 + C_2H_5NH_2.$$

Ethyl-isocyanic ether, $CNO^-C_2H_5$, is formed from chlorcyan and sodium ethoxide:

$$CNCl + NaOC_2H_5 = CNOC_2H_5 + NaCl.$$

It is a liquid insoluble in water, and not distillable without decomposition. With potassium hydroxide it breaks into potassium cyanate and alcohol ;

$$CNO^-C_2H_5 + KHO = CNOK + C_2H_5OH.$$

Ethyl mustard oil, $CSN^-C_2H_5$, is produced in a manner analogous to the methyl mustard oil. It is a colorless liquid with the odor of mustard oil, boiling at 134°. With nascent hydrogen it passes into ethylamine and methylsulphaldehyde :

$$CSN^-C_2H_5 + 2\ H_2 = CH_3S + C_2H_5(NH_2).$$

Ethyl sulphocyanide, $C_2H_5{}^-SCN$, is obtained by digestion of potassium ethylsulphate with potassium sulphocyanide. It is a liquid with an unpleasant odor, boiling at 146°. With nascent hydrogen, it yields cyanhydric acid and ethylmercaptan :

$$CNS^-C_2H_5 + H_2 = CNH + C_2H_5SH.$$

C_3 GROUP.

Propane Compounds.

All compounds that contain three carbon atoms bound to each other, are derived from the hydrocarbon $CH_3{-}CH_2{-}CH_3$, *Propane*. The diversity of the derivatives and the number of the isomers in this series is naturally greater than in the ethane series. It will only be necessary to consider the more important members of this class, since most of the compounds not mentioned here can be produced according to the analogous reactions of the corresponding members of the methane and ethane series.

The replacement of an atom of hydrogen by a mono-valent atom, or atomic group, can produce two isomeric substances, depending on whether an atom of the group CH_3 or CH_2 is substituted.

Bodies formed by substitution in the CH_3 group are called *propyl* compounds, while those arising from substitution in the CH_2 group are known as *isopropyl* compounds.

Propane is but little known. The first derivative of it is *propylene*, $CH_3{-}CH{=}CH_2$, which is formed from allyl iodide and iodohydric acid:

$$C_3H_5I + HI = C_3H_6 + I_2.$$

Also from isopropyl iodide and potassium hydroxide:

$$C_3H_7I + KOH = C_3H_6 + KI + H_2O.$$

Propylene is a gas. It unites with iodohydric acid to form isopropyl-iodide:

$$C_3H_6 + HI = C_3H_7I = CH_3{-}CHI{-}CH_3.$$

There is also a hydrocarbon of the C_3 series corresponding to acetylene, viz.,

Allylene, $CH_3{-}C{\equiv}CH$. It is formed by the action of propylene bromide on an alcoholic solution of potassium hydroxide:

$$CH_3{-}CHBr{-}CH_2Br + 2KHO = CH_3{-}C{\equiv}CH + 2\,KBr + 2\,H_2O.$$

It is a colorless gas, which, like acetylene, gives explosive precipitates with an alcoholic ammoniacal solution of cuprous chloride or silver nitrate. It unites with bromine, forming two compounds, *allylene dibromide*, $CH_3{-}CBr{=}CHBr$, and *allylene tetrabromide*, $CH_3{-}CBr_2{-}CHBr_2$.

Propyl Chloride, $CH_3{-}CH_2{-}CH_2Cl$, or C_3H_7Cl, is a colorless liquid, boiling at 47°. It is obtained from normal propyl alcohol by the action of gaseous chlorhydric acid.

Isopropyl Chloride, $CH_3{-}CHCl{-}CH_3$, or C_3H_7Cl, obtained from isopropyl alcohol. It boils at 37°. Both have a pleasant odor and resemble ethyl chloride.

Propyl bromide, $CH_3{-}CH_2{-}CH_2Br$, or C_3H_7Br, boils at 71°.

Isopropyl bromide, $CH_3{-}CHBr{-}CH_3$, or C_3H_7Br, boils at 61°.

Both are obtained from the corresponding alcohols by the action of bromhydric acid. They resemble ethyl bromide very much.

Propyl iodide, $CH_3{-}CH_2{-}CH_2I$, or C_3H_7I, boils at 102°.

Isopropyl iodide, $CH_3{-}CHI{-}CH_3$, or C_3H_7I, boils at 80°.

Both are obtained from the corresponding alcohols by the action of gaseous iodohydric acid, and are liquids resembling ethyl iodide, being colorless and having pleasant odors.

Propylene chloride, $CH_3{-}CHCl{-}CH_2Cl$, or $C_3H_6Cl_2$ is formed on the contact of propylene and chlorine. It boils at 97°. By continued action of chlorine, all the hydrogen is replaced by chlorine.

The other dichlorpropylenes are (1) $CH_3{-}CHCl{-}CH_2Cl$, boils at 97°. (2) $CH_2Cl{-}CH_2{-}CH_2Cl$, boils at 117°. (3) $CH_3{-}CH_2{-}CHCl_2$, boils at 85°. (4) $CH_3{-}CCl_2{-}CH_3$, boils at 70°. All four have the formula $C_3H_6Cl_2$.

Propyl Alcohol, $CH_3{-}CH_2{-}CH_2(OH)$, or C_3H_8O, is formed

in small amounts in the fermentation of sugar, and is hence present in crude spirit.

It can be formed synthetically from ethyl cyanide. Ethyl cyanide is converted into propionic acid by boiling with potassium hydroxide :

$$C_2H_5{-}CN + 2\,H_2O = C_2H_5{-}COOH + NH_3.$$

The propionic acid is transformed into its lime salt, which, after being well dried at 100°, is distilled with calcium formate :

$$\begin{matrix} C_2H_5COO \\ C_2H_5COO \end{matrix}\!\!>\!Ca + \begin{matrix} HCOO \\ HCOO \end{matrix}\!\!>\!Ca = \begin{matrix} C_2H_5{-}CHO \\ C_2H_5{-}CHO \end{matrix} + \begin{matrix} CaCO_3 \\ CaCO_3 \end{matrix}.$$

The propionic aldehyde which is thus obtained is converted into propyl alcohol by the action of nascent hydrogen (sodium amalgam) :

$$C_2H_5{-}CHO + H_2 = C_2H_5{-}CH_2(OH), \text{ or } CH_3{-}CH_2{-}CH_2(OH).$$

Propyl alcohol is a liquid with a pleasant alcoholic odor. It boils at 98°.

All the reactions of both propyl and isopropyl alcohols are analogous to those of methyl and ethyl alcohols. Their halogen substitutions, ethers, and esters are formed in the same manner as the corresponding derivatives of the C_2 group from ethyl alcohol.

Isopropyl Alcohol, $CH_3{-}CH(OH){-}CH_3$, or C_3H_8O, is also formed in small amounts in the alcoholic fermentation of sugar, and is hence present in crude spirits. It is usually made artificially either from glycerol or acetone.

Glycerol when heated with iodohydric acid yields isopropyl iodide :

$$C_3H_8O_3 + 5\,HI = C_3H_7I + 2\,I_2 + 3\,H_2O,$$

which when boiled with plumbic hydroxide and water gives isopropyl alcohol :

$$2\,C_3H_7I + Pb(OH)_2 = 2\,C_3H_8O + PbI_2.$$

It is formed from acetone by reduction with sodium amalgam :

$$CH_3{-}CO{-}CH_3 + H_2 = CH_3{-}CH(OH){-}CH_3.$$

It is a liquid resembling propyl alcohol. It boils at 83°. The normal propyl alcohol yields propionic aldehyde,

$CH_3{-}CH_2{-}CHO$, and propionic acid, $CH_3{-}CH_2{-}COOH$, on oxidation. By oxidation of isopropyl alcohol, however, acetone, $CH_3{-}CO{-}CH_3$, is first formed. By further oxidation, the molecule splits, giving acetic and formic acids. Owing, however, to the easy oxidizability of formic acid, acetic acid and carbonic acid are the final products. The oxidation of the alcohol, affords, therefore, a method of ascertaining whether the OH is bound to the CH_3 or the CH_2.

The first oxidation product of propyl alcohol is *Propionaldehyde,* $CH_3{-}CH_2{-}CHO$, or C_3H_6O. It can also be obtained by distilling a salt of propionic acid with a salt of formic acid. It is a colorless liquid, soluble in but not miscible with water. It boils at 49°, and has a suffocating aldehyde odor. On exposure to the air it oxidizes to propionic acid.

The first oxidation product of isopropyl alcohol is **Acetone,** *Dimethyl-ketone,* $CH_3{-}CO{-}CH_3$, or C_3H_6O. Acetone is formed by the dry distillation of many organic substances *e.g.*, sugar, tartaric acid, etc. It is a constituent of wood-spirit. It is also formed by the action of zinc methyl on acetyl chloride :

$$(CH_3)_2Zn + 2\,CH_3{-}COCl = 2\,CH_3{-}CO{-}CH_3 + ZnCl_2.$$

The best method of producing it is to submit salts of acetic acid to dry distillation :

$$\begin{matrix} CH_3{-}COONa \\ + CH_3{-}COONa \end{matrix} = \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CO + Na_2CO_3.$$

It is a limpid liquid with a peculiar odor. It boils at 58°, and is miscible with water, alcohol, and ether.

Acetone breaks on oxidation into formic (carbonic) and acetic acids. It is converted by reduction with sodium amalgam in aqueous solution into isopropyl alcohol :

$$CH_3{-}CO{-}CH_3 + 3\,O = \underset{\text{Acetic acid}}{CH_3{-}COOH} + \underset{\text{Formic acid}}{CHOOH}$$

$$CH_3{-}CO{-}CH_3 + H_2 = \underset{\text{Isopropyl alcohol}}{CH_3{-}CH(OH){-}CH_3}$$

It combines with acid alkali sulphites, forming crystalline compounds.

Chlorine acts directly on acetone with substitution of the hydrogen :

C_3H_6O, *Acetone.*

C_3H_5ClO, *Monochloracetone*, colorless liquid. Boils at 119°. It causes weeping.

$C_3H_4Cl_2O$, *Dichloracetone*, boils at 120°. Its constitution is $CHCl_2{-}CO{-}CH_3$. The compound isomeric with it, $CH_2Cl{-}CO{-}CH_2Cl$, forms colorless crystals, fusing at 43° and boiling at 172–174°.

$C_3H_3Cl_3O$, *Trichloracetone*, $CCl_3{-}CO{-}CH_3$, boils at 170–174°.

$C_3H_2Cl_4O$, *Tetrachloracetone.*

C_3HCl_5O, *Pentachloracetone*, boils at 190°.

C_3Cl_6O, *Perchloracetone*, boils at 200°.

They are liquids with powerful odors. The higher chlorinated acetones, as the trichloracetone, etc., combine with water, forming crystalline hydrates.

By the action of gaseous chlorhydric acid, or concentrated sulphuric acid, acetone is condensed, several molecules uniting to one molecule with the elimination of water. The most important of these are :

Mesityloxide, $C_6H_{10}O$, colorless liquid boiling at 130°:

$$2\,C_3H_6O - H_2O = C_6H_{10}O.$$

Phorone, $C_9H_{14}O$, fuses at 28° and boils at 196° :

$$3\,C_3H_6O - 2\,H_2O = C_9H_{14}O.$$

Mesitylene, C_9H_{12} :

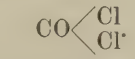
$$3\,C_3H_6O - 3\,H_2O = C_9H_{12}.$$

We shall consider these compounds in the aromatic series.

We see from the name of acetone, "dimethyl-ketone," that there are other similar bodies, or "ketones," which contain, instead of the methyls, other hydrocarbon rests. Acetone may be considered as a compound in which the two active valences of CO are satisfied by two CH_3's :


Acetone


Urea


Carbonyl chloride

One of the methods of producing acetone can easily be

varied so as to produce *mixed ketones.* Zinc methyl and acetyl chloride give acetone; zinc ethyl and acetyl chloride yield *methylethyl-ketone;* zinc ethyl and propionyl chloride form *di-ethyl-ketone,* and so on. Mixed ketones, and especially those of a higher order, can also be produced in another way. In the same manner that the distillation of an acetate affords acetone, the distillation of the salts of higher acids produce ketones of a higher order. Thus a salt of propionic acid yields on distillation *di-ethyl-ketone:*

$$\begin{matrix} C_2H_5\text{-}COONa \\ + \ C_2H_5\text{-}COONa \end{matrix} = \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!CO + Na_2CO_3.$$

By the distillation of a mixture of an acetate and a propionate, *methyl-ethyl-ketone* is obtained:

$$\begin{matrix} CH_3\text{-}COONa \\ + \ C_2H_5\text{-}COONa \end{matrix} = \begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!CO + Na_2CO_3.$$

If instead of an acetate, a formate is taken, the aldehyde of the acid is obtained, one of the free valences of the CO being neutralized by an H, the other by a hydrocarbon rest:

$$\begin{matrix} CH_3\text{-}COONa \\ HCOONa \end{matrix} = \begin{matrix} CH_3 \\ H \end{matrix}\!\!>\!CO + Na_2CO_3.$$

The compound $\begin{matrix} CH_3 \\ H \end{matrix}\!\!>\!CO$, as is evident, is $CH_3\text{-}CHO$, or C_2H_4O, aldehyde. The production of many aldehydes and alcohols of higher orders depends on this method. Ketones are therefore aldehydes in which the H of the CHO is replaced by a hydrocarbon rest. The relations are seen at once from the following formulas:

Methyl aldehyde, $CO\!<\!\begin{matrix} H \\ H \end{matrix}$.

Ethyl aldehyde, $CO\!<\!\begin{matrix} H \\ CH_3 \end{matrix}$.

Methyl ketone, $CO\!<\!\begin{matrix} CH_3 \\ CH_3 \end{matrix}$.

The ketones, like the aldehydes, are reduced by sodium amalgam. They always yield the secondary alcohols:

$$CH_3\text{-}CO\text{-}CH_3 + H_2 = CH_3\text{-}CH(OH)\text{-}CH_3.$$

An intermediate product is formed in the reduction, however, by two molecules of the ketone taking up two atoms of hydrogen forming *pinacones.*

$$2\,(CH_3)_2{=}CO + H_2 = (CH_3)_2{=}C(OH){-}C(OH){=}(CH_3)_2 = C_6H_{14}O_2.$$

The pinacones are, hence, glycols. They are characterized by their losing easily a molecule of water when treated with acids, forming *pinacolines:*

$$C_6H_{14}O_2 - H_2O = C_6H_{12}O = (CH_3)_3{\equiv}C{-}COCH_3.$$

The pinacolines are ketones. The pinacoline obtained from acetone is the *tertiary methyl-butyl-ketone.*

Ketones unite like the aldehydes with cyanhydric acid, forming cyan compounds:

$$(CH_3)_2{=}CO + HCN = (CH_3)_2{=}C\begin{matrix}\diagup\,OH\\ \diagdown\,CN\end{matrix}$$

Ketones break on oxidation into two acids of lower carbon series:

$$CH_3{-}CO{-}CH_3 + 3\,O = CH_3{-}COOH + HCOOH.$$

In this reaction the CO-group remains in combination with the lesser hydrocarbon rest:

$$C_4H_9{-}CO{-}C_2H_5 + 3\,O = C_4H_8O_2 + C_2H_5{-}COOH.$$

Propionic Acid. $CH_3{-}CH_2{-}COOH$, or $C_3H_6O_2$, is the second oxidation product of normal propyl alcohol, and can be obtained by the oxidation of it. It is also formed by boiling ethyl cyanide with potassium hydroxide:

$$C_2H_5{-}CN + KOH + H_2O = C_2H_5{-}COOK + NH_3.$$

In nature it occurs in the sweat, in the fluids of the stomach, and in the blossoms of the milfoil. It is a liquid with a sharp odor resembling that of acetic acid. It distils at 140°. It is miscible with water, but is separated as an oil floating on the surface by dissolving salts in its solution.

Chlorine, bromine, etc., substitution-products, the anhydride, $\begin{matrix}C_2H_5{-}CO\\ C_2H_5{-}CO\end{matrix}\!\!\rangle O$, propionyl chloride, $C_2H_5{-}CO{-}Cl$, as

well as many salts and esters have been produced. Their properties are easily deduced from the corresponding acetyl compounds.

Propyl glycol. There are two isomeric propyl glycols:

1) $CH_2(OH)$
CH_2
$CH_2(OH)$

2) CH_3
$CH(OH)$
$CH_2(OH)$.

The first is the *normal propyl glycol,* the second the *iso-propyl glycol.* Both are oily liquids, the former boiling at 216°, the latter at 186°. Their chlorhydrins, acetates, etc., are known.

By oxidizing the normal propyl glycol, there is produced the normal

Propyl-glycollic Acid, $CH_2(OH)^-CH_2^-COOH$, or $C_3H_6O_3$. It is a syrup very much resembling lactic acid. Its salts are, however, different from those of lactic acid. It can be produced synthetically.

Ethylene-glycol, $CH_2(OH)^-CH_2(OH)$, is converted by chlorhydric acid into ethyleneglycol hydrochloride $CH_2(OH)^-CH_2Cl$ glycol-chlorhydrin), which, in turn, by the action of potassium cyanide passes into the cyanide, $CH_2(OH)^-CH_2(CN)$. The cyanide on boiling with potassium hydroxide yields propylglycollic acid:

$$CH_2(OH)^-CH_2^-CN + KHO + H_2O = CH_2(OH)^-CH_2^-COOK + NH_3.$$

Propylglycollic acid, being a glycollic acid, is both alcohol and acid. On oxidation, the alcoholic group $CH_2(OH)$ is converted into carboxyl, $CO(OH)$, forming *malonic acid:*

$$CO(OH)^-CH_2^-CO(OH).$$

On heating, water splits out, yielding *acrylic acid,* $C_3H_4O_2$:

$$CH_2(OH)^-CH_2^-COOH = CH_2{=}CH^-COOH + H_2O.$$

By the oxidation of isopropylglycol we obtain *Isopropyl-glycollic Acid, Lactic Acid,* $CH_3^-CH(OH)^-COOH$.

Lactic acid occurs in sour milk and in many plant juices. It is formed from sugar by a peculiar fermentation known as the "lactic fermentation," and is found in many sour, fermented liquids (sauerkraut, etc.). It can be formed synthetically from aldehyde and cyanhydric acid.

If aldehyde and cyanhydric acid are treated with concentrated chlorhydric acid, a compound is formed which contains the elements of both aldehyde and cyanhydric acid:

$$CH_3{}^-CHO + CNH = CH_3{}^-CH(OH){}^-CN.$$

As it is a cyanide, the N can be replaced by the group O(OH), thus forming lactic acid:

$$CH_3{}^-CH(OH){}^-CN + 2\,H_2O = CH_3{}^-CH(OH){}^-COOH + NH_3.$$

In the same manner, therefore, that propylglycollic acid is formed from ethylene glycol, lactic acid is produced from aldehyde, *i.e.*, from the hypothetical ethylidene glycol:

$$CH_3{}^-CH\begin{matrix}OH\\OH\end{matrix}.$$

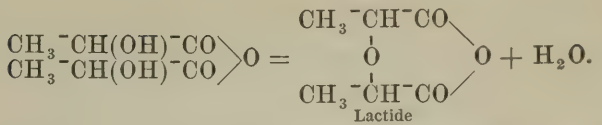
It is usually made by allowing sugar to stand several days with putrid cheese, chalk, and water at a temperature of 30–35°. Calcium lactate is formed, from which the lactic acid is set free by sulphuric acid.

Lactic acid is a syrup with a sour taste. It is miscible with water, alcohol, and ether. On distillation, it gives off water and is converted into the anhydride, $C_2H_{10}O_5$:

$$\begin{matrix}CH_3{}^-CH(OH){}^-COOH\\+\ CH_3{}^-CH(OH){}^-COOH\end{matrix} = \underset{\text{Lactic anhydride}}{\begin{matrix}CH_3{}^-CH(OH){}^-CO\\CH_3{}^-CH(OH){}^-CO\end{matrix}}\!\!>O + H_2O.$$

The formation of the anhydride takes place partly at ordinary temperatures.

At 260° another molecule of water splits out of lactic anhydride, forming *Lactide*, $C_6H_8O_4$:



Lactide forms rhombic tablets fusing at 124.5°, but little soluble in water. In contact with water it gradually changes back into lactic acid.

The most important salts of lactic acid are:

Magnesium lactate, $(C_3H_5O_3)_2Mg$. It is obtained by neutralizing lactic acid with magnesium carbonate. Small bitter crystals difficultly soluble in water.

Zinc lactate, $(C_3H_5O_3)_2Zn$, is obtained by neutralization of lactic acid with zinc carbonate. Acicular crystals soluble in 58 parts of cold water.

Ferrous lactate, $(C_3H_5O_3)_2Fe$, yellowish-green crystalline powder difficultly soluble in water.

Both of the isomeric lactic acids are homologues of glycollic acid. They are part alcohol and part acid, and possess the same peculiarities as the glycollic acid. They form ester-acids, $CH_3{-}CH(OC_2H_5){-}COOH$, *ethyl-lactic acid*, and esters, $CH_3{-}CH(OH){-}COOC_2H_5$, *ethyl lactic ester*. When the alcoholic hydroxyl is replaced by NH_2, amic acids are formed, as $CH_3{-}CH(NH_2){-}COOH$, *lactamic acid*, or *alanine*, while the replacement of the hydroxyl of the carboxyl by NH_2 produces amides, as *lactamide*, $CH_3{-}CH(OH){-}CONH_2$.

The isomeric propyl-glycollic acids show marked differences on oxidation. The normal acid oxidizes to malonic acid, $COOH{-}CH_2{-}COOH$, the ordinary lactic acid to pyroracemic acid, $CH_3{-}CO{-}COOH$, which, however, is immediately oxidized into acetic and formic acids. The differences in the zinc salts are still more striking. Zinc propylglycollate crystallizes with 4 H_2O, and is easily soluble in water, while zinc lactate crystallizes with 3 H_2O, and is difficultly soluble in water.

In the juice of the muscles there exists an acid called *sarcolactic acid*. It is a mixture of normal propylglycollic acid with an optically active modification of lactic acid known as *paralactic acid*. This acid turns the plane of polarized light to the right. Its zinc salt differs from that of lactic acid by crystallizing with 2 H_2O, and being easily soluble in water.

Malonic Acid, $COOH^{-}CH_2^{-}COOH$, or $C_3H_4O_4$, is the oxidation product of the normal propylglycollic acid, or ethylenelactic acid. It is made from cyanacetic acid, $CH_2\langle^{CN}_{COOH}$.

By the action of potassium cyanide, monochloracetic acid is converted into cyanacetic acid, and this by boiling passes into malonic acid :

$$\begin{matrix} CN \\ | \\ CH_2 \\ | \\ COOH \end{matrix} + HKO + H_2O = \begin{matrix} COOH \\ | \\ CH_2 \\ | \\ COOK \end{matrix} + NH_3.$$

It is crystalline and soluble in water, alcohol, and ether. It fuses at 132°, and at higher temperatures decomposes into acetic and carbonic acids. It is a dibasic acid and forms two series of salts, acid and neutral.

Its *ethyl ester*, $CH_2(COOC_2H_5)_2$, has, like acetic ester, the power of taking up one atom of sodium, yielding a compound which easily decomposes with chlorides, bromides, etc., and affords a convenient method for the synthesis of complicated dibasic acids, *e.g.* :

$$CHNa(COOC_2H_5)_2 + C_2H_5Br = NaBr + \underset{\text{Ethylmalonic ethyl ester}}{C_2H_5^{-}CH(COOC_2H_5)_2}.$$

Pyroracemic acid, $CH_3^{-}CO^{-}COOH$, or $C_3H_4O_3$, is produced by the distillation of racemic acid :

$$\underset{\text{Racemic acid}}{C_4H_6O_6} = C_3H_4O_3 + CO_2 + H_2O.$$

It is also formed by decomposing acetyl cyanide, $CH_3^{-}CO^{-}CN$, with chlorhydric acid. It is a colorless liquid with a piercing odor, miscible with water, alcohol, and ether. At 165° it boils with partial decomposition. It is monobasic. Nascent hydrogen converts it into lactic acid :

$$CH_3^{-}CO^{-}COOH + H_2 = CH_3^{-}CH(OH)^{-}COOH,$$

just as acetone is converted into isopropyl alcohol.

We have as yet considered only those oxidation-products of propane in which the hydrogen of one or two carbon atoms has been oxidized. If the oxidation takes place at all three of the carbon atoms, we obtain as the first representative of the class of compounds :

Glycerol, Glycerine, $CH_2(OH)^-CH(OH)^-CH_2(OH)$, $C_3H_8O_3$. Glycerol occurs in almost all the vegetable and animal fats and oils. The fats and oils are, in fact, glyceric esters of monobasic acids of high carbon content (oleïc, palmitic, stearic, etc.), the hydrogen of the three hydroxyls being replaced by the acid rests. A small amount of glycerol is formed during the alcoholic fermentation of sugar (about 3% of the sugar fermented). It is made commercially by decomposing fats with superheated steam.

It is a colorless syrup with a sweet taste. Its sp. gr. is 1.28, and it is miscible with alcohol and water. It attracts moisture from the air. When perfectly pure, it distils at 290° without decomposition, but when not quite pure, it decomposes at about 275° into acroleine (p. 123) and water. It distils easily with steam.

Since glycerol contains three alcoholic hydroxyls, it forms three series of esters with acids. The acetic esters, or *acetins*, are as follows:

Monacetin, $CH_2(OH)^-CH(OH)^-CH_2O(C_2H_3O)$,
Diacetin, $CH_2(OH)^-CHO(C_2H_3O)^-CH_2O(C_2H_3O)$,
Triacetin, $CH_2O(C_2H_3O)^-CHO(C_2H_3O)^-CH_2O(C_2H_3O)$.

The stearic and oleïc esters are called *stearin* and *olein*. They will be considered under the fats. In the same manner that glycerol forms esters, or compound ethers, with acid rests, it yields ethers with alcoholic rests, as, for instance:

Mon-ethylglycerol, $C_3H_5(OH)_2(OC_2H_5)$,
Di-ethylglycerol, $C_3H_5(OH)(OC_2H_5)_2$,
Tri-ethylglycerol, $C_3H_5(OC_2H_5)_3$.

We have seen that a mixture of glycerol and oxalic acid yields formic acid when heated at 110°. This reaction depends on the formation of the primary glycerol oxalic ester, which on heating to 110° evolves carbonic acid and passes into formic acid:

$$\underset{\text{Glycerol oxalic ester}}{CH_2(OH)^-CH(OH)^-CH_2O^-CO^-COOH}$$

$$= \underset{\text{Glycerol formic ester}}{CH_2(OH)^-CH(OH)^-CH_2O^-CHO} + CO_2$$

The formic ester thus formed breaks into glycerol and formic acid by boiling with water:

$$CH_2(OH)^-CH(OH)^-CH_2O^-CHO + H_2O$$
$$= CH_2(OH)^-CH(OH)^-CH_2(OH) + CH_2O_2.$$

If glycerol is dropped into a cooled mixture of concentrated nitric and sulphuric acids, *glycerol nitric ester*, or *nitrin*, wrongly called *nitro-glycerine*, is formed:

$$CH_2(ONO_2)^-CH(ONO_2)^-CH_2(ONO_2),\ \textit{Trinitrin}.$$

It is a light-yellow oil, which explodes violently on concussion. It is used as a blasting agent. Mixed with $\frac{1}{4}$ of its weight of infusorial earth, it bears the name of *dynamite*. The other nitrins are also known.

By mixing glycerol with concentrated sulphuric acid, *glycerol sulphuric ester*, $C_3H_5(OH)_2SO_4H$ is produced. With phosphoric anhydride, *glycerol phosphoric ester* is formed, $C_3H_5(OH)_2H_2PO_4$. The latter acid is also formed from the decomposition of *lecithin*, a substance occurring in the brain and in the yolks of eggs.

On treatment with chlorhydric acid, glycerol yields chlorhydrins. The longer the action, the higher will be the substitution:

Monochlorhydrin, $C_3H_5(OH)_2Cl$,
Dichlorhydrin, $C_3H_5(OH)Cl_2$,
Trichlorhydrin, $C_3H_5Cl_3$.

We see that this reaction is the same as the one by which the alcohols were converted into chlorides:

$$CH_4O + HCl = CH_3Cl + H_2O,$$
$$C_3H_8O_3 + HCl = C_3H_7ClO_2 + H_2O,$$

the only difference being that with glycerol the reaction takes place in three phases, and the three products of it can be isolated:

Monochlorhydrin, $C_3H_7ClO_2$, is formed by heating glycerol saturated with chlorhydric acid gas. It is an oily liquid boiling at 220°.

Dichlorhydrin, $C_3H_6Cl_2O$, is produced in two isomeric forms by continued heating of glycerol with chlorhydric acid. The first

modification, $CH_2Cl^-CH(OH)^-CH_2Cl$, boils at 172°–173° ; the second, $CH_2Cl^-CHCl^-CH_2OH$, at 182°–183°. Both are liquids with agreeable odors, and difficultly soluble in water. By the action of potassium hydroxide, HCl is split out, forming *epichlorhydrin*, C_3H_5ClO.

Trichlorhydrin, $C_3H_5Cl_3$, is formed by the action of phosphorus pentachloride on dichlorhydrin. It is a liquid resembling chloroform. It boils at 158°.

Corresponding to the chlorhydrins, there are *bromhydrins* and *chlorbromhydrins*, etc.

If glycerol is digested with iodohydric acid, an inverse substitution, *i.e.*, a reduction, is effected, and *isopropyl iodide*, $CH_3^-CHI^-CH_3$, is obtained.

The iodohydric acid converts the glycerol first into isopropyl alcohol :

$$CH_2(OH)^-CH(OH)^-CH_2(OH) + 4\,HI = CH_3^-CH(OH)^-CH_3 + 2\,H_2O + 2\,I_2.$$

The isopropyl alcohol is, however, at once changed into isopropyl iodide by the further action of the acid:

$$CH_3^-CH(OH)^-CH_3 + HI = CH_3^-CHI^-CH_3 + H_2O.$$

When glycerol is mixed with phosphorus di-iodide, PI_2, heat is strongly evolved and allyl iodide, C_3H_5I, propylene, C_3H_6, and iodine are formed:

$$CH_2(OH)^-CH(OH)^-CH_2(OH) + PI_2 = CH_2{=}CH^-CH_2I + PH_3O_3 + I.$$

In the same manner that poly-glycols are formed from ethylene glycol, *poly-glycerols* are obtained from glycerol. They are simply ethers of glycerol.

By careful oxidation, glycerol passes into *glyceric acid*.

Glyceric Acid, $CH_2(OH)^-CH(OH)^-COOH$, or $C_3H_6O_4$, is a monobasic acid, yielding crystallizable salts with metals. The free acid does not crystallize.

Tartronic acid may be regarded as the next oxidation product of glycerol, although it is not obtained from glycerol.

Tartronic acid, $\begin{matrix}\text{COOH}\\|\\\text{CH(OH)}\\|\\\text{COOH}\end{matrix}$, or $C_3H_4O_5$. It is obtained from nitrotartaric acid (p. 136) and is a dibasic acid forming large colorless crystals. It fuses at 150°, decomposing into carbonic acid, water, and *glycolide:*

$$C_2H_2O_2, \begin{matrix}\text{CO}\\|\\\text{CH}_2\end{matrix}\!\!>\!\text{O}.$$

We may consider mesoxalic acid as the last oxidation product of glycerol:

Mesoxalic acid, $\begin{matrix}\text{COOH}\\|\\\text{C(OH)}_2\\|\\\text{COOH}\end{matrix}$, or $C_3H_4O_5$, is obtained by treating dibrom-malonic acid, $COOH^{-}CBr_2{}^{-}COOH$, with silver oxide. It crystallizes in colorless, deliquescent prisms containing water of crystallization. It is dibasic and very unstable, oxidizing easily to oxalic and carbonic acids:

$$\begin{matrix}\text{COOH}\\|\\\text{(OH)}_2\\|\\\text{COOH}\end{matrix} + \text{O} = \begin{matrix}\text{COOH}\\|\\\text{COOH}\end{matrix} + \text{H}_2\text{O}.$$

A reaction of glycerol with phosphorus di-iodide has just been noticed, by which allyl iodide, $CH_2{=}CH^{-}CH_2I$, or C_3H_5I, is produced. If the iodine in this iodide is replaced by hydroxyl (which can be effected by the well-known method of converting the iodide into an ester and then decomposing it by an alkali), the representative of a new class of alcohols is obtained. They contain a pair of doubly bound carbon atoms, and hence have two atoms of hydrogen less than the ordinary alcohols. They behave with the various reagents in the same manner as the ordinary alcohols, suffer the same substitutions, etc. In the presence of nascent hydrogen they take up two molecules of hydrogen. They also combine with halogens, viz.:

$$C_3H_5OH + Br_2 = CH_2Br^{-}CHBr^{-}CH_2OH.$$

This class of compounds is called *unsaturated.* Those belonging to the C_3 series are the more important, and are de-

rived from propylene, $CH_2{=}CH{-}CH_3$. They bear the name *allyl*, because some of them occur in members of the *allium* family.

Allyl Iodide, $CH_2{=}CH{-}CH_2I$, or C_3H_5I, is obtained by the action of phosphorus di-iodide on glycerol. It is a colorless liquid with the odor of leeks. It boils at 101°.

When treated with chlorine or bromine, iodine separates, and *allyl trichloride*, $C_3H_5Cl_3$ (trichlorhydrin), or *allyl tribromide*, $C_3H_5Br_3$ (tribromhydrin), are formed. The latter gives with potassium cyanide *allyl tricyanide*, $C_3H_5(CN)_3$, which when boiled with potassium hydroxide affords *tricarballylic acid*, $C_3H_5(COOH)_3$. By digestion with a silver salt (the oxalate is usually employed) silver iodide and allyl oxalic ester are formed. The latter is decomposed by ammonia into allyl alcohol and oxamide :

$$\begin{matrix} CO(OC_3H_5) \\ | \\ CO(OC_3H_5) \end{matrix} + 2\,NH_3 = \begin{matrix} CO(NH_2) \\ | \\ CO(NH_2) \end{matrix} + 2\,C_3H_5OH.$$

Allyl Alcohol, $CH_2{=}CH{-}CH_2OH$, or C_3H_6O. Allyl alcohol is isomeric with both propyl aldehyde and acetone. It is found among the products of the dry distillation of wood. It can be made, as just shown, from allyl iodide, or by heating glycerol with oxalic acid at 200°.

In this case the formic ester of glycerol is formed, which at 200° breaks into carbonic acid and allyl alcohol, water being eliminated :

$$C_3H_5(OH)_2{-}O{-}CHO = C_3H_5OH + CO_2 + H_2O.$$

Allyl alcohol is a colorless liquid with a peculiar and penetrating odor. It boils at 97°, is combustible, and miscible with water. It dissolves sodium with evolution of hydrogen, forming *sodium alloxide*, C_3H_5ONa, which with allyl iodide gives the *allyl ether*, $C_3H_5{-}O{-}C_3H_5$.

Allyl ether is a liquid boiling at 83°, and not miscible with water.

Oxidizing agents convert allyl alcohol into the corresponding aldehyde (acroleine) and acid (acrylic acid). The oxidation of the alcohol is a method but poorly suited for the

production of acroleine or acrylic acid, since the greater part of the allyl alcohol is completely decomposed, breaking into acetic and formic (carbonic) acids.

Acroleine, Acrole, $CH_2{=}CH{-}CHO$, or C_3H_4O. Acroleine is made by heating glycerol to which glacial phosphoric acid or primary potassium sulphate has been added for the purpose of promoting the reaction. The glycerol loses two molecules of water :

$$C_3H_8O_3 = C_3H_4O + 2\,H_2O.$$

It is a liquid boiling at 52°. Its odor is extremely unpleasant and attacks the mucous membranes very strongly. In water it is difficultly soluble, swimming like a layer of oil upon its surface. It changes gradually, when kept in closed vessels, into a polymeric body called *disacryl,* a white, flocculent substance, the molecular weight of which is not known. It unites directly with chlorhydric acid, forming a body known as *acroleine hydrochloride,* but which is really $CH_3{-}CHCl{-}CHO$. With sodium amalgam it does not form allyl alcohol, but propyl alcohol :

$$CH_2{=}CH{-}CHO + 2\,H_2 = CH_3{-}CH_2{-}CH_2OH.$$

As acroleine is an aldehyde, it gives all the characteristic reactions of aldehydes, taking up oxygen very easily and passing into the corresponding acid. By boiling it with a silver salt a silver mirror is obtained, and also the silver salt of

Acrylic Acid, $CH_2{=}CH{-}COOH$, or $C_3H_4O_2$. Acrylic acid is obtained in the free state by decomposing its silver salt with hydrogen sulphide. It is a liquid boiling at about 140°, with a piercing acid odor. It is a monobasic acid. Its salts are mostly crystalline. On oxidation, it breaks into acetic acid and formic or carbonic acids. Sodium amalgam reduces it to propionic acid :

$$C_3H_4O_2 + H_2 = C_3H_6O_2.$$

It unites easily with bromine, forming dibrompropionic acid, and with iodohydric acid to mono-iodopropionic acid.

By distilling allyl iodide with potassium cyanide we obtain *Allyl cyanide*, $C_3H_5{-}CN$. It occurs in commercial mustard-oil, and is a colorless liquid boiling at 118°. With potassium hydroxide it evolves ammonia and passes into *crotonic acid:*

$$C_3H_5{-}CN + KHO + H_2O = C_3H_5{-}COOK + NH_3.$$

It is therefore called *crotonic nitrile.*

By digesting allyl iodide with silver cyanide we obtain *Allyl isocyanide*, $C_3H_5{-}NC$, which is a liquid with an offensive odor, boiling at 106°. Acids decompose it into formic acid and allyl-amine :

$$C_3H_5NC + 2\,H_2O = C_3H_5NH_2 + CH_2O_2.$$

Allyl Mustard-Oil, **Mustard-Oil** *par excellence, Allyl Thiocarbyl-amine*, $C_3H_5{-}N{=}CS$. Mustard-oil does not exist ready formed in nature, but is produced by a peculiar fermentation when the seeds of the black mustard are moistened with water.

After removing the oil from the black mustard seeds by pressing, they are moistened with water and allowed to remain moist several days, after which they are distilled with water. The mustard-oil can also be produced from allyl iodide and potassium sulphocyanate.

Mustard-oil is a colorless liquid boiling at 148°. It has a piercing odor which causes weeping. In water it is insoluble. It produces blisters on the skin.

Ammonia converts it into *allylsulpho-urea*, or *thiosinamine*,

$$CS\begin{matrix}\diagup NH{-}C_3H_5\\ \diagdown NH_2\end{matrix}.$$

By heating with lead oxide and water it yields *di-allylurea*, or *sinapoline*,

$$CO\begin{matrix}\diagup NH{-}C_3H_5\\ \diagdown NH{-}C_3H_5\end{matrix}.$$

Allyl sulphocyanate, $C_3H_5{-}SCN$, is formed by the action of potassium

sulphocyanate on allyl iodide in the cold. It is a liquid with a peculiar odor, which on distillation is converted into mustard-oil.

Allyl Sulphide, Garlic Oil, $\begin{matrix} C_3H_5 \\ C_3H_5 \end{matrix}\!\!>\!S$, is contained in the bulbs of the garlic (*allium sativum*), and is obtained by distilling them with water. It can also be produced from allyl iodide and potassium sulphide, K_2S:

$$2\,C_3H_5I + K_2S = (C_3H_5)_2S + 2\,KI.$$

It is a colorless liquid with the odor of garlic. It boils at 140° and forms crystalline compounds with several metallic salts, as mercuric chloride.

We shall only mention a few of the remaining compounds of the propane series, since their formation and their more important properties can be deduced from the corresponding compounds of the ethane series.

Propylamine, $CH_3{-}CH_2{-}CH_2(NH_2)$, boiling at 50°.

Isopropylamine, $CH_3{-}CH(NH_2){-}CH_3$, boils at 32°.

Both are alkaline liquids with ammoniacal odors. They form well-characterized salts with acids.

Amidopropionic acid, alanine, $CH_3{-}CH(NH_2){-}COOH$, is obtained by boiling aldehyde-ammonia and cyanhydric acid with chlorhydric acid:

$$CH_3{-}CH(NH_2)(OH) + HCN + H_2O = CH_3{-}CH(NH_2){-}COOH + NH_3.$$

Alanine crystallizes in rhombic prisms, which on heating decompose into ethylamine and carbonic acid:

$$C_3H_7NO_2 = C_2H_7N + CO_2.$$

Uric acid and its derivatives properly belong to the C_3 group, as they do not contain more than three carbon atoms bound to each other, but a clearer understanding of this complicated class can be obtained by considering them later on as a class by themselves.

C_4 GROUP.

Butane Compounds.

In the butane group there are of course a greater number and variety of isomers than in the preceding groups. The base of the series itself, *Butane*, exists in two modifications, depending upon whether an H of a CH_3 or a CH_2, of propane,

$$CH_3\text{-}CH_2\text{-}CH_3,$$

is substituted by a CH_3. We have, therefore :

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3, \quad \textit{Butane},$$

and

$$\begin{array}{l} CH_3\text{-}CH\text{-}CH_3, \\ \quad\quad | \\ \quad\quad CH_3 \end{array} \qquad \textit{Isobutane}.$$

It is also evident that the result of a substitution of an H in the butanes by an element, or atomic complex, will depend on whether the substitution takes place in a CH_3 or a CH_2 of propane, or a CH_3 or a CH in the isopropane. We see hence that in case of a monosubstitution of the butanes there are four isomers. The number of isomers increases rapidly when several hydrogen atoms are substituted.

We have not space to note all the possible substitutions of this series, many of which have not yet actually been obtained, and must be content, therefore, to consider only the more important ones.

1) *Normal butyl chloride*, $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2Cl$, or C_4H_9Cl, is obtained from the corresponding alcohol by the action of gaseous chlorhydric acid gas. It boils at 78°.

2) *Pseudobutyl chloride*, or *secondary butyl chloride*,

$CH_3{-}CH_2{-}CHCl{-}CH_3$, or C_4H_9Cl.

It boils at 66°.

3) *Isobutyl chloride*, $CH(CH_3)(CH_2Cl)(CH_3)$, or C_4H_9Cl. It boils at 69°.

4) *Tertiary butyl chloride*, $CCl(CH_3)_3$, or C_4H_9Cl. It boils at 50–51°.

All four of them are colorless liquids with pleasant odors.

1) *Normal butyl iodide*, $CH_3{-}CH_2{-}CH_2{-}CH_2I$, obtained like the chloride. Boils at 130°.

2) *Secondary butyl iodide*, $CH_3{-}CH_2{-}CHI{-}CH_3$, boils at about 80°.

3) *Isobutyl iodide*, $CH(CH_3)(CH_2I)(CH_3)$, boils at 121°.

4) *Tertiary butyl iodide*, $CI(CH_3)_3$, boils at 99°.

1) *Normal butyl alcohol, propyl carbinol*, $CH_3{-}CH_2{-}CH_2{-}CH_2OH$, C_4H_9OH, or $C_4H_{10}O$. It is obtained from the corresponding butyric acid by the method described under propyl alcohol.

Calcium butyrate is mixed with calcium formate and submitted to dry distillation. The butyraldehyde is separated from the distillate and transformed into butyl alcohol by the action of nascent hydrogen.

It can also be produced from glycerol by a peculiar fermentation.

It is a colorless liquid with an odor partly like alcohol and partly like fusel oil. It boils at 116°, and is soluble in water, although not miscible with it in all proportions. Its properties are analogous to those of the preceding alcohols. On oxidation, it passes into butyraldehyde and normal butyric acid.

2) *Secondary butyl alcohol, ethyl-methyl-carbinol*,

$CH_3{-}CH_2{-}CH(OH){-}CH_3$, C_4H_9OH, $C_4H_{10}O$.

It is formed from erythrol by the action of iodohydric acid, by a reaction analogous to the formation of isopropyl alcohol from glycerol (compare p. 120):

$$\underset{\text{Erythrol}}{C_4H_{10}O_4} + 7\,HI = \underset{\substack{\text{Sec. butyl}\\\text{iodide}}}{C_4H_9I} + 4\,H_2O + 6\,I.$$

$$C_4H_9I + KOH = C_4H_9OH + KI.$$

It is also made indirectly. Dichlorether, $CH_2Cl\text{-}CHCl\text{-}O\text{-}C_2H_5$, is converted, by treatment with zinc ethyl, into ethylmonochlorether,

$$CH_2Cl\text{-}CH(C_2H_5)\text{-}O\text{-}C_2H_5.$$

This compound is then transformed into butyl iodide and ethyl iodide by treating with iodohydric acid :

$$CH_2Cl\text{-}CH(C_2H_5)\text{-}O\text{-}C_2H_5 + 4\,HI = CH_3\text{-}CHI\text{-}C_2H_5 + C_2H_5I + HCl + H_2O + I_2.$$

The butyl iodide is then converted into the alcohol by the action of moist silver oxide :

$$2\,C_2H_5\text{-}CHI\text{-}CH_3 + Ag_2O + H_2O = 2\,C_2H_5\text{-}CH(OH)\text{-}CH_3 + 2\,AgI.$$

The formula $C_2H_5\text{-}CHI\text{-}CH_3$ is $CH_3\text{-}CH_2\text{-}CHI\text{-}CH_3$, or secondary butyl iodide, and the alcohol obtained from it is hence

$$CH_3\text{-}CH_2\text{-}CH(OH)\text{-}CH_3.$$

Secondary butyl alcohol is a colorless liquid with a pleasant odor. It boils at 98°. It is soluble in water, but not miscible with it. It loses the elements of water easily and passes into butylene, $CH_3\text{-}CH{=}CH\text{-}CH_3$. By oxidation it is transformed into the ketone:

$$CH_3\text{-}CH_2\text{-}CO\text{-}CH_3, \text{ or } CO\begin{matrix}CH_2\text{-}CH_3\\CH_3\end{matrix},$$

methyl-ethyl ketone. By further oxidation it breaks into two molecules of acetic acid.

3) **Isobutyl Alcohol,** *Isopropyl Carbinol,*

$$CH\begin{matrix}CH_3\\CH_3\\CH_2OH\end{matrix}, \quad C_4H_9OH, \quad C_4H_{10}O,$$

is formed in small amounts in the alcoholic fermentation of sugar, and hence occurs in crude spirits.

In the rectification of crude spirits, it goes over, after the ethyl alcohol has been distilled, with the fusel oil, from which it is separated by fractional distillation.

It is a liquid which boils at 107°, and is soluble in, but not miscible with water. Its odor resembles that of fusel oil. By oxidation it is converted first into isobutyraldehyde and then into isobutyric acid.

4) *Tertiary butyl alcohol, trimethyl carbinol,*

$$C(OH)\begin{cases}CH_3\\CH_3\\CH_3\end{cases},\ C_4H_9OH,\ C_4H_{10}O.$$

It is made from acetyl chloride and zinc methyl.

By allowing the mixture to stand some time at a gentle heat, a compound of one molecule of acetyl chloride with two molecules of zinc methyl separates in crystals. Water decomposes this compound into tertiary butyl alcohol, zinc hydroxide, and methane:

$$2\left[\underset{\text{Acetyl chloride}}{CH_3{-}COCl} + 2\,\underset{\text{Zinc methyl}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!Zn}\right] + 6\,H_2O = 2\,\underset{\text{Tertiary butyl alcohol}}{CH_3{-}C(OH)\begin{matrix}<CH_3\\CH_3\end{matrix}} + 4\,CH_4 + 3\,Zn(HO)_2 + ZnCl_2.$$

The alcohol is an oily liquid solidifying at the ordinary temperature in crystals. It boils at 82°, and has a characteristic camphor-like odor. It breaks easily into pseudobutylene, $CH_2{=}C\begin{matrix}<CH_3\\CH_3\end{matrix}$, and water. On oxidation it yields chiefly acetic and propionic acids besides carbonic acid, *i.e.*, oxidized formic acid.

We have now become familiar with three kinds of alcohols. The first are the proper, *normal,* or *primary alcohols.* They are characterized by containing the group CH_2OH, and give on oxidation an aldehyde and an acid. As the OH replaces an H of the group CH_3, there remain two H's which can be oxidized. To this class all the normal alcohols and also the isobutyl alcohol belong. The second group of alcohols is called *secondary.* They are characterized by the group CHOH. The hydroxyl replaces an H in a CH_2, thus leaving only one oxidizable H. On oxidation they do not give an aldehyde and an acid, but yield a ketone, which by continued oxidation breaks into two acids of lower carbon content, the molecule breaking at the carbon atom which binds the hydroxyl:

$$\underset{\text{Secondary butyl alcohol}}{CH_3{-}CH_2{-}CH(OH){-}CH_3}\ \text{yields acetic acid.}$$

Isopropyl alcohol and the secondary butyl alcohol belong

to this class. They lose the elements of water easily, yielding a hydrocarbon of the formula C_nH_{2n}, *e.g.:*

$$CH_3{-}CH_2{-}CH(OH){-}CH_3 = CH_3{-}CH{=}CH{-}CH_3 + H_2O.$$

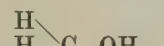
The third class of alcohols, which are known as the *tertiary*, is characterized by the group C–OH, formed by the replacement of an H in the group CH. The hydroxylated carbon does not bind any oxidizable hydrogen, and by oxidation they break at once into acids of lower carbon content:

$C(OH)\begin{cases}CH_3\\CH_3\\CH_3\end{cases}$ yields acetic and formic acids.

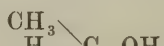
The tertiary alcohols have also the tendency to drop out the elements of water and pass into hydrocarbons of the formula C_nH_{2n}, *e.g.:*

$$CH_3{-}\underset{\displaystyle CH_3}{C}(OH){-}CH_3 = CH_3{-}\underset{\displaystyle CH_3}{C}{=}CH_2 + H_2O.$$

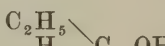
The most convenient method of naming the alcohols is to consider them as derivatives of methyl alcohol, or *carbinol*, viz.:



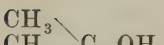
$CH_3 . OH$
Carbinol
Methyl alcohol



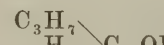
$C_2H_5 . OH$
Ethyl alcohol
Methyl carbinol



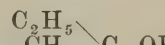
$C_3H_7 . OH$
Propyl alcohol
Ethyl carbinol



$C_3H_7 . OH$
Isopropyl alcohol
Dimethyl carbinol



$C_4H_9 . OH$
Butyl alcohol
Propyl carbinol



$C_4H_9 . OH$, etc.
Sec. butyl alcohol
Methylethyl carbinol

The other bonds of the hydroxylated carbon atom must, of course, be satisfied by hydrocarbon rests:

$^{-}CH_2^{-}OH$ binds one carbon atom, by one bond;

$^{=}CH^{-}OH$ binds two carbon atoms, each by one bond;

$\equiv C^{-}OH$ binds three carbon atoms, each by one bond.

Certain of the isomeric alcohols can be transformed into each other. The primary pass into the secondary, and these into the tertiary. In some cases a primary alcohol can be transformed into another isomeric primary alcohol.

Among the four butyl alcohols described, there are only two which yield aldehydes. The normal butyl alcohol gives the *normal butyraldehyde*, $CH_3^{-}CH_2^{-}CH_2^{-}CHO$, or C_4H_8O, a liquid with an aldehyde-like odor, boiling at 75°. Isobutyl alcohol yields *isobutyraldehyde*, $CH_3^{-}CH\langle^{CH_3}_{CHO}$, which boils at 61° and resembles the other aldehyde. From the secondary butyl alcohol a ketone is derived, *methyl-ethyl ketone* (p. 128), a liquid with an ethereal odor, which boils at 81°. No oxidation-derivative containing four carbon atoms is possible from the tertiary alcohol. The two aldehydes give isomeric acids on further oxidation, viz.: *butyric acid* and *isobutyric acid*.

Butyric Acid, $CH_3^{-}CH_2^{-}CH_2^{-}COOH$, or $C_4H_8O_2$. Butyric acid occurs with other acids as a glycerol ester (butyrin) in butter. It exists also in the perspiration, in the liquid of the muscles, and in the carob bean. It is formed by the lactic fermentation of sugar, and is hence found in *Sauerkraut*, sour pickles, etc. By the oxidation of the normal butyl alcohol it is also formed.

It is obtained by the fermentation of sugar. Sugar is mixed with chalk, putrid cheese and water, and allowed to stand several weeks at 30–35°. The calcium lactate, which is at first formed, by continued fermentation evolves carbonic acid and water, and passes into calcium butyrate:

$$\underset{\text{Lactic acid}}{2\,C_3H_6O_3} = \underset{\text{Butyric acid}}{C_4H_8O_2} + 2\,CO_2 + 2\,H_2O.$$

Butyric acid is a colorless, strongly acid liquid, with an odor resembling that of acetic acid. It boils at 163.5°. When it contains a trace of ammonia, it has an offensive odor of perspiration. It is miscible in water, but is separated on dissolving salts therein. Its salts are crystalline. It forms with

acetates double salts, which consist of one molecule of butyric acid combined with one molecule of acetate.

Isobutyric Acid, $CH_3{-}CH\begin{cases}CH_3\\COOH\end{cases}$, or $C_4H_8O_2$. Isobutyric acid is formed by the oxidation of isobutyl alcohol. It is also obtained by boiling isopropyl cyanide with potassium hydroxide:

$$CH_3{-}CH\begin{cases}CN\\CH_3\end{cases} + KHO + H_2O = CH_3{-}CH\begin{cases}COOK\\CH_3\end{cases} + NH_3.$$

Its properties resemble those of butyric acid. It boils at 154°. Its lime and lead salts differ from the corresponding ones of butyric acid. *Calcium butyrate,* $(C_3H_7COO)_2Ca$, is more easily soluble in cold water than in hot, while *calcium isobutyrate* is more easily soluble in hot than in cold water. *Plumbic butyrate,* $(C_3H_7CO_2)_2Pb$, is crystalline, while *plumbic isobutyrate* solidifies to a resinous amorphous mass.

There are six possible glycols derivable from the two butanes:

1) $CH_2(OH)$–CH_2–CH_2–$CH_2(OH)$

2) $CH_2(OH)$–$CH(OH)$–CH_2–CH_3

3) $CH_2(OH)$–CH_2–$CH(OH)$–CH_3

4) CH_3–$CH(OH)$–$CH(OH)$–CH_3

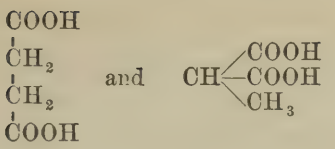
5) $CH\begin{cases}CH_2(OH)\\CH_2(OH)\\CH_3\end{cases}$

6) $C(OH)\begin{cases}CH_2(OH)\\CH_3.\\CH_3\end{cases}$

Of these six, there are four known.

Of the five possible butylglycollic acids, or hydroxybutyric acids, three are known, viz.: *α-Hydroxybutyric acid,* $CH_3{-}CH_2{-}CH(OH){-}COOH$, *β-hydroxybutric acid,* $CH_3{-}CH(OH){-}CH_2{-}COOH$, *acetonic acid,* $C(OH)\begin{cases}COOH\\CH_3\\CH_3\end{cases}$, and *Hydroxyisobutyric acid,* $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C(OH){-}COOH$.

Both of the possible dicarboxylic acids of the C_4 group are known:



The former is *succinic acid*, the latter *isosuccinic acid*.

Succinic Acid, $COOH^{-}CH_2^{-}CH_2^{-}COOH$, or $C_4H_6O_4$. This acid exists in amber, in many plants, and in the animal organism.

It is formed in small amounts in the alcoholic fermentation of sugar, and also by the reduction of malic acid (p. 134) and tartaric acids by iodohydric acids :

$$\underset{\text{Malic acid}}{C_4H_6O_5} + 2\,HI = C_4H_6O_4 + H_2O + I_2$$

$$\underset{\text{Tartaric acid}}{C_4H_6O_6} + 4\,HI = C_4H_6O_4 + 2\,H_2O + 2\,I_2.$$

It can also be produced from ethylene cyanide, $C_2H_4(CN)_2$:

$$\begin{matrix} CH_2^{-}CN \\ | \\ CH_2^{-}CN \end{matrix} + 4\,H_2O = \begin{matrix} CH_2^{-}COOH \\ | \\ CH_2^{-}COOH \end{matrix} + 2\,NH_3$$

It is generally made by the distillation of amber.

Succinic acid crystallizes in monoclinic prisms, which fuse at 180° and boil at 235°, with partial formation of the anhydride. It is soluble in water and hot alcohol. Its vapors are irritating, causing coughing. It is a dibasic acid, forming two series of salts. The succinates of the alkaline metals are easily soluble in water, while those of the other metals are difficultly soluble, or altogether insoluble.

With phosphorus pentachloride it gives *succinyl chloride*, $\begin{matrix} CH_2^{-}COCl \\ | \\ CH_2^{-}COCl \end{matrix}$, an oily liquid boiling at 190°, which fumes in the air and is decomposed by water, and with ammonia yields succinamide.

Succinamide, $\begin{matrix} CH_2^{-}CO(NH_2) \\ | \\ CH_2^{-}CO(NH_2) \end{matrix}$, crystallizes in white needles, which are

easily soluble in water. On heating, ammonia splits out, forming *succinimide*, $\begin{matrix}CH_2\text{-}CO\\ |\\ CH_2\text{-}CO\end{matrix}\!\!>\!NH$, which crystallizes in colorless needles, containing one molecule of H_2O. It fuses at 125°, and boils at 287°.

Bromine reacts with succinic acid, replacing hydrogen. *Monobromsuccinic acid*, $C_2H_3Br(CO_2H)_2$, crystallizes in warty concretions. *Dibromsuccinic acid*, $C_2H_2Br_2(CO_2H)_2$, is also a crystalline body.

By repeated distillations, succinic acid is converted into *Succinic Anhydride*, $\begin{matrix}CH_2\text{-}CO\\ |\\ CH_2\text{-}CO\end{matrix}\!\!>\!O$, which forms colorless crystals fusing at 120° and boiling at 250°. On boiling with water it passes back into the acid :

$$\begin{matrix}CH_2\text{-}CO\\ |\\ CH_2\text{-}CO\end{matrix}\!\!>\!O + H_2O = \begin{matrix}CH_2\text{-}COOH\\ |\\ CH_2\text{-}COOH\end{matrix}$$

Succinic acid is converted into normal butyric acid by reduction :

$$\begin{matrix}CH_2\text{-}COOH\\ |\\ CH_2\text{-}COOH\end{matrix} + 3\,H_2 = \begin{matrix}CH_2\text{-}CH_3\\ |\\ CH_2\text{-}COOH\end{matrix} + 2\,H_2O.$$

Isosuccinic acid, methylmalonic acid, $CH_3\text{-}CH\!<\!\begin{matrix}COOH\\ COOH\end{matrix}$, or $C_4H_6O_4$. This acid is produced from cyanpropionic acid :

$$CH_3\text{-}CH\!<\!\begin{matrix}CN\\ COOH\end{matrix} + 2\,H_2O = CH_3\text{-}CH\!<\!\begin{matrix}COOH\\ COOH\end{matrix} + NH_3.$$

It forms crystals which fuse at 130°, and are more easily soluble in water than ordinary succinic acid. At 150° it falls into propionic and carbonic acids.

The hydrogen in both the CH_2-groups of succinic acid can be replaced by hydroxyls, thus yielding a series of dicarboxylic acids containing more oxygen than succinic acid.

Malic Acid, $\begin{matrix}CH(OH)\text{-}COOH\\ |\\ CH_2\text{-}COOH\end{matrix}$. This acid occurs in many

sour fruits, as apples, gooseberries, mountain-ash berries, etc. It can be made from succinic acid by boiling bromsuccinic acid with silver oxide, and from tartaric acid by heating with iodohydric acid. It is usually obtained from the berries of the mountain ash.

It is a difficultly crystallizable, solid mass, which is deliquescent, easily soluble in water and alcohol, fuses at 100°, and decomposes at a higher temperature. It is dibasic, and forms two series of salts. It stands in the same relation to succinic acid as glycollic acid does to acetic acid. Iodohydric acid converts it into succinic acid. When digested with potassium chromate, carbonic acid is eliminated, and it passes into malonic acid:

$$\begin{matrix}CH(OH)^{-}COOH\\ |\\ CH_2{}^{-}COOH\end{matrix} + O_2 = \begin{matrix}COOH\\ |\\ CH_2{}^{-}COOH\end{matrix} + CO_2 + H_2O.$$

It suffers a peculiar fermentation in contact with yeast, yielding succinic, acetic, and butyric acids.

The malic acid occurring in nature polarizes to the left, while that made from succinic acid is optically inactive. These physical differences appear even more sharply defined in the case of tartaric acid.

One of the amido-derivatives of malic acid is worthy of attention, viz., *Asparagine*, $\begin{matrix}CH_2{}^{-}CO(NH_2)\\ |\\ CH(NH_2)^{-}COOH\end{matrix}$, or $C_4H_8N_2O_3$.

It occurs in asparagus, liquorice, and in the germs of many plants, and crystallizes in transparent prisms containing one molecule of water. It is soluble in water, and combines with both acids and bases. In contact with putrid cheese, it is reduced to succinic acid. Nitrous acid converts it into malic acid:

$$\begin{matrix}CH_2{}^{-}CO(NH_2)\\ |\\ CH(NH_2)^{-}COOH\end{matrix} + N_2O_3 = \begin{matrix}CH_2{}^{-}COOH\\ |\\ CH(OH)^{-}COOH\end{matrix} + H_2O + 2\,N_2.$$

By boiling with acids or alkalis, the amido-group is replaced by the hydroxyl-group, forming *aspartic*, or *amidosuccinic acid:*

$$\begin{matrix}CH_2\text{-}CO(NH_2)\\ |\\ CH(NH_2)\text{-}COOH\end{matrix} + H_2O = \begin{matrix}CH_2\text{-}CO(OH)\\ |\\ CH(NH_2)\text{-}COOH\end{matrix} + NH_3.$$

Both asparagine and aspartic acid are optically active.

From the isobromsuccinic acid, *isomalic acid*, $CH_3\text{-}C(OH)\langle^{CO_2H}_{CO_2H}$, has been obtained by the action of silver oxide.

Tartaric Acid, $\begin{matrix}CH(OH)\text{-}COOH\\ |\\ CH(OH)\text{-}COOH\end{matrix}$, or $C_4H_6O_6$.

Tartaric acid occurs in many fruits, particularly in grapes. It is formed by the oxidation of milk-sugar, and by boiling dibromsuccinic acid with silver oxide.

Young wine on standing deposits a thick crust on the sides of the casks, which consists of the acid tartrates of potassium and calcium. Both of the salts were originally in solution in the must; but, as the wine becomes richer in alcohol, the salts which are insoluble in alcohol are precipitated. This deposit is called crude *argol*, and is the material from which tartaric acid is made.

Tartaric acid crystallizes in monoclinic prisms, easily soluble in alcohol and water. It forms two series of salts. It tastes strongly acid. When heated in the air, it gives an odor of burnt sugar.

It fuses at 135°, forming, on cooling, a gummy mass, *metatartaric acid*. The salts of this acid are converted into salts of ordinary tartaric acid by boiling with water. On heating tartaric acid to 150°, water is eliminated, and *ditartaric acid*, $C_8H_{10}O_{11}$, an amorphous deliquescent mass is formed. On further heating to 180° more water is eliminated, and *tartrelic acid*, or *tartaric anhydride*, $C_8H_8O_{10}$, is produced. On being submitted to dry distillation, it yields a large number of products, of which we shall only mention *pyroracemic acid*, $C_3H_4O_3$, and *pyrotartaric acid*, $C_5H_8O_4$. With nitric acid it forms a nitric ester, called *nitrotartaric acid*, $\begin{matrix}CH(ONO_2)\text{-}COOH\\ |\\ CH(ONO_2)\text{-}COOH\end{matrix}$, which decomposes on evaporation of its aqueous solution into carbonic acid, nitrous anhydride, and tartronic acid, $C_3H_4O_5$ (p. 121).

Tartaric acid on being heated with iodohydric acid is reduced to succinic acid :

$$C_4H_6O_6 + 2\,HI = C_4H_6O_5 + H_2O + I_2$$
$$C_4H_6O_6 + 4\,HI = C_4H_6O_4 + 2\,H_2O + 2\,I_2.$$

The most important tartrates are :

Hydrogen Potassium Tartrate, Argol, Cream of Tartar, $C_4H_5KO_6$. It is difficultly soluble in cold water. Its formation is a characteristic test for tartaric acid.

Hydrogen Ammonium Tartrate, $C_4H_5(NH_4)O_6$, is also difficultly soluble in cold water. The neutral salt is easily soluble.

Potassium Tartrate, $C_4H_4K_2O_6$, forms crystals easily soluble in water. It is changed into the acid salt by boiling with water.

Potassium Sodium Tartrate, Rochelle Salts, $C_4H_4KNaO_6\,4H_2O$. This salt is formed by saturating bitartrate of potash with sodium carbonate. It forms large transparent rhombic columns, which are easily soluble in water.

Calcium Tartrate, $C_4H_4CaO_4 + 4\,H_2O$, is almost insoluble in cold water. It is soluble in cold potassium hydroxide solution, and is precipitated by boiling. This behavior of the calcium salt is characteristic of tartaric acid, and is used to detect its presence.

Potassium Antimony Basic Tartrate, Potassium Antimonyl Tartrate, Tartar Emetic, $C_4H_4(SbO)KO_4 + \frac{1}{2}\,H_2O$. It is obtained by boiling potassium bitartrate with antimony oxide. Colorless rhombohedrons and octahedrons, which are quite soluble in cold water, and cause nausea. It loses a molecule of water at 200°, yielding the compound $C_4H_2KSbO_6$.

In this salt, $C_4H_4K(SbO)O_6$, one of the hydrogen atoms of the carboxyl is replaced by K, the other by the group SbO, *antimonyl.*

There are four physically different modifications of tartaric acid, the chemical properties of which, however, are identical.

1) *Inactive Tartaric Acid,* which has no effect on the ray of polarized light.

The tartaric acid obtained from dibromsuccinic acid belongs under this head. It is also formed by the oxidation of sorbine, and together with racemic acid by heating ordinary tartaric acid to 165°. On heating with water to 175°, it is partly converted into racemic acid. It is easily soluble in water. Its acid potassium salt is also easily soluble.

2) *Racemic Acid,* which does not act on the polarized ray, but can be converted into optically active acids. If ammonium sodium racemate is allowed to crystallize, two sets of crystals are formed which are exactly the same, except that one is the reflected image of the other, the hemihedral faces being developed on opposite sides of the crystals. By separating these crystals and converting them into the free acid, we find that one kind gives the

3) *Dextrotartaric Acid,* which turns the polarized ray to the right, and the other the

4) *Levotartaric Acid,* which turns the ray of polarized light the same number of degrees to the left.

The ordinary tartaric acid is the dextrotartaric acid. Sometimes racemic acid in the form of its potassium and calcium salts is also found in argol.

Racemic acid is formed by the oxidation of mannite, dulcite, and mucic acid. Also by the action of cyanhydric acid and chlorhydric acid on glyoxal. An addition-product of glyoxal with cyanhydric acid is formed, which is decomposed by the chlorhydric acid :

$$CHO\text{-}CHO + 2\,HCN = CN\text{-}CH(OH)\text{-}CH(OH)\text{-}CN,$$
$$CN\text{-}CH(OH)\text{-}CH(OH)\text{-}CN + 4\,H_2O = CO_2H\text{-}CHOH\text{-}CHOH\text{-}CO_2H + 2\,NH_3.$$

It is also formed, together with inactive tartaric acid, by heating dextrotartaric acid with water at 175°. It crystallizes in long, rhombic, efflorescent crystals. Its salts differ but little from those of dextrotartaric acid.

A trihydric alcohol, or butylic glycerol, is not known. A tetrahydric alcohol, which is the richest alcohol in oxygen in this series, is, however, known.

Erythrol, Erythrite, $\begin{matrix} CH(OH)\text{-}CH_2(OH) \\ | \\ CH(OH)\text{-}CH_2(OH) \end{matrix}$, or $C_4H_{10}O_4$,

occurs in nature. It is obtained from erythrin, a constituent of certain lichens. It forms large, transparent crystals, with a sweet taste, which fuse at 120°, and are easily soluble in water. With nitric acid it give a nitric ester, $C_4H_6(ONO_2)_4$, analogous to nitroglycerol, and which is violently explosive.

Iodohydric acid converts it into secondary butyl iodide (as glycerol into isopropyl iodide). It can be oxidized to erythric acid, $\begin{matrix}CH(OH)\text{-}COOH\\ |\\ CH(OH)\text{-}CH_2(OH)\end{matrix}$, which stands to it in the same relation as glyceric acid to glycerol.

Although tartaric acid has not been produced from erythrol, it may be regarded as the dicarboxylic acid of it, and thus stands in the same relation to it as oxalic acid to glycol.

There are several oxygen derivatives of the C_4-group which are unsaturated compounds, and which stand in the same relation to the corresponding butyl compounds as do the allyl compounds to the propyl derivatives.

Crotonaldehyde, C_4H_6O, is produced by the condensation of ethyl aldehyde. Its constitution is $CH_3\text{-}CH{=}CH\text{-}CHO$.

$$CH_3\text{-}CHO + CH_3\text{-}CHO = CH_3\text{-}CH{=}CH\text{-}CHO + H_2O.$$

It is a liquid with a piercing odor, boiling at 105°. By oxidation it is converted into *crotonic acid*, $CH_3\text{-}CH{=}CH\text{-}COOH$, which fuses at 72° and boils at 184°. This acid can also be obtained from allyl cyanide and potassium hydroxide.

Besides the solid crotonic acid, there is the *isocrotonic acid*,

$$CH_2{=}CH\text{-}CH_2\text{-}COOH,$$

a liquid which boils at 172°, and which during distillation is partly decomposed into solid crotonic acid and *methacrylic acid*,

$$CH_2{=}C\begin{matrix}CH_2\\ COOH,\end{matrix}$$

which boils at 160° and solidifies at 16°.

If malic acid is heated to 150°, water is eliminated and it is converted into

Fumaric acid, $\begin{matrix}CH\text{-}COOH\\ \|\\ CH\text{-}COOH\end{matrix}$, or $C_4H_4O_4$.

$$\begin{matrix} CH(OH)\text{-}COOH \\ | \\ CH_2\text{-}COOH \end{matrix} = \begin{matrix} CH\text{-}COOH \\ \| \\ CH\text{-}COOH \end{matrix} + H_2O.$$

Fumaric acid occurs in many plants, as Iceland moss, *fumaria officinalis*, etc. It crystallizes in small needles, which are difficultly soluble in cold water, easily in alcohol. It volatilizes at 200°, and is converted into the isomeric maleïc acid.

Maleïc acid, $\begin{pmatrix} CH_2\text{-}COOH \\ | \\ C\text{-}COOH \end{pmatrix}$. It fuses at 130°, and is easily soluble in water. It is converted back into fumaric acid when heated for some time at 130°. Both of these acids give succinic acid by reduction. They are both characterized by the small amount of hydrogen they contain.

The constitution of this acid was formerly supposed to be $CH_2{=}C\begin{matrix} COOH \\ COOH \end{matrix}$, but the first formula better represents certain of its reactions. The existence of a di-valent or unsaturated carbon atom in the molecule, has, however, not yet been established with certainty.

Of the remaining compounds of this group we shall mention only:

Butylamine, $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2(NH_2)$, or $C_4H_9(NH_2)$, which boils at 75°, and

Isobutylamine, $CH_3\text{-}CH\begin{matrix} CH_3 \\ CH_2(NH_2) \end{matrix}$, or $C_4H_9(NH_2)$, which boils at 70°.

Both are liquids with ammoniacal odors and basic properties. They form crystalline salts.

C_5 GROUP.

Pentane Compounds.

THE saturated hydrocarbon C_5H_{12}, which forms the base of the *Pentane* or *Amyl* series, exists in three isomeric modifications :

$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_3,$$

$$CH_3{-}CH_2{-}CH\begin{matrix}CH_3\\CH_3\end{matrix},$$

and

$$CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}{-}CH_3.$$
$$CH_3$$

The number of isomeric substitutions in this series is hence much greater than in the preceding ones. Only a few of them are known, and the constitution of many of these has not been determined with certainty.

There are eight possible alcohols, of which seven are known ; three of them are primary, three secondary, and one tertiary.

1) *Normal amyl alcohol, butyl-carbinol,*

$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2(OH), \text{ or } C_5H_{12}O,$$

is made from normal valerianic acid. It is a colorless liquid with a suffocating odor. It boils at 137°. This alcohol yields a *chloride*, $C_5H_{11}Cl$, which boils at 107°, a *bromide* (b. p. 129°), and an *iodide* (b. p. 155°).

On oxidation, it is converted into normal valeraldehyde and normal valerianic acid.

2) *Ordinary Amyl Alcohol, Isobutyl-Carbinol,*

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH\text{-}CH_2\text{-}CH_2(OH), \text{ or } C_5H_{12}O.$$

This alcohol is the chief constituent of *fusel oil.* It is formed during the alcoholic fermentation of sugar, and is separated from the crude spirit by distillation. It is a colorless liquid boiling at 131.4°. Its odor is disagreeable and causes coughing. The *chloride* produced from it, $C_5H_{11}Cl$, boils at 99°, the *iodide* at 147°.

Nearly all derivatives have been produced from this alcohol which have been obtained from ethyl alcohol. We shall omit the description of them, since their chief properties will appear on comparison with the corresponding compounds of the ethane series.

By oxidation it is converted into valeraldehyde and valerianic acid, the properties of which are of course different from those of the normal aldehyde and acid.

3) *Secondary butyl-carbinol.* Fusel oil contains a second amyl alcohol which differs from the preceding chiefly in its polarizing to the left. It has the constitution, $CH_3\text{-}CH_2\text{-}CH\!<\!\begin{matrix}CH_3\\CH_2OH\end{matrix}$, and boils at 127°.

4) *Isopropylmethyl-carbinol,* $CH_3\text{-}CH(OH)\text{-}CH\!<\!\begin{matrix}CH_3\\CH_3\end{matrix}$, or $C_5H_{12}O$, is a secondary alcohol.

It is formed by the reduction of isopropylmethyl-ketone, and is a liquid difficultly soluble in water, boiling at 113°.

5) *Propylmethyl-carbinol,* $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH(OH)\text{-}CH_3$, or $C_5H_{12}O$, boils at 119°.

6) *Diethyl-carbinol,* $C_2H_5\text{-}CH(OH)\text{-}C_2H_5$, or $C_5H_{12}O$, boils at 117°.

7) *Ethyldimethyl-carbinol, amylene hydrate,* $CH_3\text{-}CH_2\text{-}C(OH)\text{-}CH_3$, with CH_3 on the $C(OH)$, or $C_5H_{12}O$, boils at 103°. This alcohol yields only acetic acid on oxidation.

The following aldehydes are known :

1) *Normal Valeraldehyde,* $CH_3(CH_2)_3\text{-}CHO$, or $C_5H_{10}O$, boiling at 102°, and

2) *Ordinary Valeraldehyde,* $(CH_3)_2CH^-CH_2^-CHO$, or $C_5H_{10}O$, boiling at 92°.

Both of these aldehydes are liquids possessing the characteristic suffocating odor of ordinary aldehyde.

Three of the four possible acids are known.

1) *Normal Valerianic Acid,* $CH_3^-CH_2^-CH_2^-CH_2^-COOH$, or $C_5H_{10}O_2$.

This acid is produced by boiling butyl cyanide with alcoholic potassium hydroxide. It is somewhat soluble in water, boils at 185°, and has an odor resembling butyric acid. The properties of both the acid and its salts differ from those of the following acids and salts.

2) **Ordinary Valerianic Acid,**

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH^-CH_2^-COOH, \text{ or } C_5H_{10}O_2.$$

This acid occurs in the root of the valerian, and, together with butyric acid, in putrid cheese. It is made either from the valerian root, or by oxidation of ordinary amyl alcohol. It is a liquid boiling at 175°, and is lighter than water. Its odor resembles that of putrid cheese. The hydrated acid contains one molecule of water and boils at about 165°. It forms crystalline salts.

The more important salts of valerianic acid are the following :

Bismuth valerianate, $Bi(OH)_2C_5H_9O_2$ (a basic salt constituted analogously to the basic bismuth nitrate). It is a white powder insoluble in water, and has the odor of valerianic acid.

Zinc valerianate, $Zn(C_5H_9O_2)_2$, is made by dissolving zinc carbonate in valerianic acid. It forms white crystals difficultly soluble in cold water. They have a sweet taste and an odor of valerianic acid.

3) *Methyl-ethyl-acetic acid.* The secondary butylcarbinol gives an acid on oxidation which differs from the above valerianic acid in polarizing strongly to the right. Its constitution is probably $\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!CH^-COOH$, methylethylacetic acid.

4) *Tri-methyl-acetic acid*, $\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\!\!>\!C\text{-}COOH$, or $C_5H_{10}O_2$, is obtained by digestion of tertiary butyl iodide with potassium cyanide, and decomposition of the cyanide, which is formed, by potassium hydroxide :

$$CH_3\text{-}\underset{\underset{CH_3}{|}}{C}\text{-}CH_3 + KCN = CH_3\text{-}\underset{\underset{CH_3}{|}}{C}(CN)\text{-}CH_3 + KI$$

$$CH_3\text{-}\underset{\underset{CH_3}{|}}{C}(CN)\text{-}CH_3 + KHO + H_2O = CH_3\text{-}\underset{\underset{CH_3}{|}}{C}(COOK)\text{-}CH_3 + NH_3.$$

It is a solid mass fusing at 34° and boiling at 161°.

There are a number of glycols and glycollic acids known in this series. Three dicarboxylic acids of the formula, $C_5H_8O_4$, have been obtained:

1) *Glutaric acid*, $CO_2H\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CO_2H$, is formed by the decomposition of the normal propylene cyanide :

$$CN\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CN.$$

It forms large, easily soluble crystals which fuse at 97°.

2) *Pyrotartaric acid*, $CH_3\text{-}CH\!\!<\!\!\begin{matrix}COOH\\CH_2\text{-}CO_2H\end{matrix}$, is produced by the decomposition of the ordinary propylene cyanide, $CH_3\text{-}CH(CN)\text{-}CH_2(CN)$, and also by the dry distillation of tartaric acid. It forms small transparent crystals fusing at 112°.

3) *Ethylmalonic acid*, $CH_3\text{-}CH_2\text{-}CH\!\!<\!\!\begin{matrix}COH_2\\COH_2\end{matrix}$, is obtained by the distillation of cyanbutyric acid. It fuses at 112°, and at 160° breaks into carbonic and butyric acids.

Among the unsaturated compounds of this series are :

Angelic acid, $C_5H_8O_2$, which occurs in the angelica-root. It crystallizes in limpid columns which fuse at 45° and boil at 190°. It is but slightly soluble in cold water.

Methylcrotonic, or tiglic acid, $C_5H_8O_2$, occurs in croton-oil and in Roman camomile-oil. It crystallizes in prisms or tablets, fusing at 64° and boiling at 198°.

Allylacetic acid, $C_5H_8O_2$, is a liquid boiling at 182°.

C_6 GROUP.

Hexane Compounds.

THE compounds of the C_6 group are still less completely known, and their constitutions are but little understood.

This series contains a class of compounds of the highest importance in the processes of life. They are called the *carbhydrates*, since nearly all of them contain hydrogen and oxygen in the proportions necessary to form water.

The normal hexyl alcohol exists as a butyric ester in the seeds of the *Heracleum giganteum*. It boils at 158°. A secondary hexyl alcohol is obtained by the action of silver oxide on the iodide produced by treating mannite with iodohydric acid. It boils at 137°. A series of tertiary hexyl alcohols, viz., dimethylpropyl-carbinol (b. p. 115°), dimethylisopropyl-carbinol (b. p. 113°), diethylmethyl-carbinol (b. p. 120°), have been produced by the action of zinc methyl on butyryl chloride, isobutyryl chloride. and zinc ethyl on ethyl chloride. (Compare the production of trimethylcarbinol, p. 129.)

The most important monobasic acid of the series is :

Capronic Acid, $C_6H_{12}O_2$, which occurs in butter and other fats. It boils at 205° and is difficultly soluble in water.

Leucic Acid, $C_6H_{12}O_3$, a glycollic acid, is also worthy of notice. Its amido-acid, which stands in the same relation to it as glycocoll to ethylglycollic acid, is called **Leucin :**

$$C_6H_{13}NO_2 = C_5H_{10}(NH_2)COOH.$$

Leucin occurs in the pancreas, saliva, etc., and is a decomposition-product of albuminous bodies. It forms white leaflets, fusing at 170°, soluble in water. On fusion with potassium

hydroxide, it evolves hydrogen and ammonia, forming potassium carbonate and valerianate :

$$C_6H_{13}NO_2 + 3\,KHO = K_2CO_3 + C_5H_9KO_2 + NH_3 + 2\,H_2.$$

One of the most important acids of this series is

Citric Acid, $C_6H_8O_7$. It is a tricarboxylic acid, and hence tribasic. It occurs in lemons and other acid fruits, and is obtained from the juice of lemons. It forms large, limpid crystals, containing one molecule of water, soluble in four parts of water and in alcohol. In moist air it is deliquescent. Its aqueous solution on standing decomposes with the formation of mould.

It is produced synthetically from dichloracetone, $CH_2Cl{-}CO{-}CH_2Cl$, which on treatment with cyanhydric and chlorhydric acids is converted into *dichloracetonic acid*, $CH_2Cl{-}\underset{\displaystyle COOH}{C(OH)}{-}CH_2Cl$ (vide p. 132), which is transformed into *dicyanacetonic acid* by means of potassium cyanide,

$$CN{-}CH_2{-}\underset{\displaystyle COOH}{C(OH)}{-}CH_2{-}CN.$$

By decomposing this acid with chlorhydric acid, citric acid,

$$CO_2H{-}CH_2{-}\underset{\displaystyle CO_2H}{C(OH)}{-}CH_2{-}CO_2H,$$

is obtained.

On heating above 150°, it gives up water, leaving *aconitic acid* (f. p. 140°), which on further heating evolves carbonic acid, yielding two isomeric acids, viz., *citraconic acid*, $C_5H_6O_4$, deliquescent, rhombic octahedrons fusing at 80°, and *itaconic acid*, $C_5H_6O_4$, large rhombic prisms fusing at 160°. These two dicarboxylic acids, which belong to the C_5 series, can be converted one into the other. Citric acid yields, on treatment with dilute nitric acid, *mesaconic acid*, $C_5H_6O_4$, which forms thin prisms fusing at 200°. By treating itaconic acid with chlorhydric acid and decomposing the addition-product with water, a fourth isomeric acid, fusing at 70°, *paraconic acid*, $C_5H_6O_4$, can be obtained.

Citric acid being a tribasic acid yields three series of salts. The salts of the alkalis are easily soluble in water. Those of

the other metals, particularly neutral salts, are difficultly soluble. The following are the more important :

Calcium citrate, $Ca_3(C_6H_5O_7)_2$, is a white, crystalline powder difficultly soluble in cold water. It is entirely insoluble in hot water, and hence is precipitated from its cold saturated solution on boiling. This is a characteristic test for citric acid.

Magnesium citrate, $Mg_3(C_6H_5O_7)_2$, is obtained by neutralizing citric acid with magnesium carbonate. It is a crystalline mass, slowly but largely soluble in water.

Ferric citrate, $Fe_2(C_6H_5O_7)_2$, is produced by dissolving ferric hydroxide in citric acid. It forms a brownish-red mass easily soluble in water. It unites with ammonium citrate to a double salt, which is also a reddish-brown, amorphous mass easily soluble in water.

The following hexahydric hexyl alcohol is of importance.

Mannite, $C_6H_{14}O_6$, is largely diffused throughout the vegetable kingdom. It exists in large amounts in manna, the dried sap of the manna-ash (*Fraxinus ornus*). It stands in intimate relation to the sugars, and can be obtained from them by reduction :

$$C_6H_{12}O_6 + H_2 = C_6H_{14}O_6.$$

It crystallizes in prisms or needles which fuse at 166°, lose water at 200°, and on stronger heating decompose entirely. In contact with cheese and chalk, it decomposes by standing at 40° into alcohol, hydrogen and lactic, butyric and carbonic acids.

It unites with acids to esters. On digestion with iodohydric acid it gives secondary hexyl iodide :

$$C_6H_{14}O_6 + 11\,HI = C_6H_{13}I + 6\,H_2O + 5\,I_2.$$

It yields a nitric ester with nitric acid, *Nitromannite*, $C_6H_8(ONO_2)_6$, which crystallizes in needles, fuses at 108°, and explodes at 120°. On oxidation it passes into *mannitic acid*, $C_6H_{12}O_7$, and *saccharic acid*, $C_6H_{10}O_8$.

Dulcite, $C_6H_{14}O_6$, is also a hexahydric alcohol, and is isomeric with mannite. It forms large crystals. Its reactions are similar to those of mannite. It fuses at 188° and is decomposed at a higher temperature. With nitric acid it yields *nitrodulcite*, $C_6H_8(NO_2)_6$. Oxidation converts it into *mucic acid*, $C_6H_{10}O_8$.

Saccharic and *Mucic Acids*, $C_6H_{10}O_8$, are formed by the oxidation of many sugars and gums. Saccharic acid does not crystallize and is deliquescent. Mucic acid is crystalline and almost insoluble in water. They are both diabasic acids.

Following mannite are two sugar-like substances containing one molecule of water less, viz., *Quercite* and *Pinite*, $C_6H_{12}O_5$. Both are crystalline and decompose on heating. Quercite occurs in acorns, pinite in the resins of the *Pinus lambertiana* (California).

The carbhydrates will be considered later on as a class by themselves.

The higher carbon groups contain but a few members; we shall take them up without classification by groups. Their constitution is mostly unknown.

Normal Heptyl Alcohol, Œnanthylic Alcohol, $C_7H_{16}O$, is made from œnanthaldehyde. It boils at 177°.

Œnanthaldehyde, Œnanthole, $C_7H_{14}O$, is produced by the dry distillation of castor-oil. It boils at 154°.

Œnanthylic Acid, $C_7H_{14}O_2$, is formed by the oxidation of castor-oil. It is almost insoluble in water and boils at 223°.

Secondary Octyl Alcohol, Capryl Alcohol, $C_8H_{18}O$, is made from castor-oil. Is an oil boiling at 181°.

Caprylic Acid, $C_8H_{16}O_2$, occurs with capronic acid. It crystallizes under 15°, boils at 234°, and is almost insoluble in water.

Pelargonic Acid, $C_9H_{18}O_2$, occurs in geranium-oil. It fuses at 12°, is almost insoluble in water, and boils at 254°.

Capric Acid, $C_{10}H_{20}O_2$, occurs with capronic and caprylic

acids. It is a crystalline mass, having the odor of perspiration. It fuses at 30° and boils at 270°.

There are several other acids of high carbon content which occur in fats and oils. The fats and oils are, almost without exception, mixtures of neutral glycerol esters of certain monobasic acids of high carbon content. The acids are obtained from these esters, or *Glycerides*, by *saponification, i.e.*, by decomposing them with an alkali. The alkali unites with the acid, while the glycerol is set free. They can also be decomposed by superheated steam. The following acids have been isolated:

Lauric Acid, $C_{12}H_{24}O_2$, obtained from the fat of various bay-trees. It fuses at 44°.

Myristic Acid, $C_{14}H_{28}O_2$, obtained from nutmeg-butter. It crystallizes in needles fusing at 54°.

Palmitic Acid, $C_{16}H_{32}O_2$, **Stearic Acid**, $C_{18}H_{36}O_2$, and **Oleïc Acid**, $C_{18}H_{34}O_2$, in the form of glycerides, constitute the majority of fats. Palmitic acid fuses at 62°, stearic acid at 69°, while oleïc acid is a liquid at ordinary temperatures. It solidifies at 4° and fuses at 14°. Nitrous anhydride solidifies it, converting it into an isomeric modification which fuses at 44°, and is known as *elaïdic acid.*

After the three acids have been freed from the glycerol, they are separated in the following manner: The oleïc acid is obtained by strong pressure. The palmitic acid is separated from the stearic acid by repeated crystallizations, or fractional precipitation. The fractional precipitation is effected by converting the acids into their potassium salts and precipitating with an insufficient amount of chlorhydric acid. The fat acids, which are partially precipitated, are again converted into their potassium salts, and again partially precipitated. This operation is repeated until the precipitated acids show a constant fusing point. By this method of partial precipitation stearic acid is obtained first.

Stearine candles are a mixture of palmitic and stearic acids. In the cavities of the skulls of certain whales a fat occurs

called **Spermaceti.** This substance is not a glyceride, but the palmitic ester of a monohydric alcohol, *Cetyl Alcohol*, $C_{16}H_{34}O$, which fuses at 55°. Among the waxes there are also esters of monohydric alcohols. *Chinese wax*, for instance, consists chiefly of the ester of *Ceryl Alcohol*, $C_{27}H_{56}O$, with *Cerotic Acid*, $C_{27}H_{54}O_2$, and is hence ceryl cerotic ester, $C_{27}H_{55}(C_{27}H_{53}O_2)$. Beeswax consists chiefly of the palmitic ester of *Myricyl Alcohol*, $C_{30}H_{62}O$.

Linoleïc acid, $C_{16}H_{28}O_2$, which occurs as a glyceride in many drying oils, as linseed, poppy, hemp, nut, etc., is similar to oleïc acid, but is not altered by nitrous anhydride. *Ricinoleïc acid*, which occurs as a glyceride in castor-oil, is an oil solidifying at 0°. It is converted by nitrous anhydride into *ricinelaïdic acid*, fusing at 50°, and by dry distillation is decomposed into œnanthol and œnanthylic acid.

Fats.

The fats occurring in nature are, as we have already seen, mostly mixtures of the glycerides of palmitic acid, $C_{16}H_{32}O_2$, stearic acid, $C_{18}H_{36}O_2$, and oleïc acid, $C_{18}H_{34}O_2$. They are largely distributed in the animal and vegetable kingdoms. In animals they are generally found under the skin, around the intestines, and on the muscles. In plants they exist in the seeds. In the pure state they are colorless and without odor or taste. Usually, however, they possess both odor and taste, owing to a slight decomposition which has taken place, and are also colored yellow from the presence of a small amount of impurity.

At ordinary temperatures the fats are either liquid or solid, a condition which is caused by the different relations existing between the amounts of glycerol oleïc ester (*oleïn*) and the glycerol esters, of palmitic and stearic acids (*palmitin* and *stearin*) in them. The solid fats, according to their consistence, are known as tallow, butter, lard, etc., while the liquid fats are called oils. All solid fats fuse under 100°.

The fats are insoluble in water, difficultly soluble in cold alcohol, and easily soluble in ether. They form a spot on paper and wood which does not vanish, and which is called a "grease-spot." They can be distilled without change at about 300°, but are completely decomposed at a higher temperature, breaking into numerous hydrocarbons and various acids,

among which is carbonic acid, and producing many other substances, a number of which possess extremely disagreeable odors, *e.g.*, acrol. The fats are all specifically lighter than water, and hence float on its surface.

The fats are decomposed by the alkalis and alkaline earths into glycerol and the fat acids, the latter uniting with the alkalis, or alkaline earths to form salts. The fatty acid salts of the alkalis (potassium and sodium), are called *soaps*. The fats are also decomposed by oxides of zinc and lead, the metallic salts thus obtained being known as *plasters*.

The fats generally suffer a change when exposed to the air. Some of them, even when chemically pure, turn gradually into a transparent solid mass. They are then said to "dry" (*drying oils*). In doing this they take up oxygen and pass into a higher state of oxidation. The drying oils always contain, besides the ordinary glycerides, the glycerol esters of unsaturated acids of higher carbon content, which usually contain less hydrogen in relation to the carbon than oleïc acid. These unsaturated glycerides take up oxygen from the air and become solid.

Some of the fats, on the other hand, keep without change when pure. As they generally contain foreign impurities, however, particularly albuminous matters, etc., they suffer, after a time, a kind of fermentation by which the fat acids are set free, and thus impart their odor and taste to the fats, causing them to become "rancid." The drying oils are prevented from drying by these impurities. Concentrated sulphuric acid does not act on the fats, but quickly destroys the albuminous matters. To free the fats from their accompanying impurities, they are therefore shaken with 3–4% of concentrated sulphuric acid. The albuminous matters are carbonized, and, sinking to the bottom, can easily be removed. This operation is termed "refining." Burning oils made from fats must be purified in this manner, else the impurities will carbonize in the wick and stop it up.

The principal animal fats are human fat, beef tallow, mutton tallow, and lard. They all consist of mixtures of palmitin, stearin, and oleïn:

$C_3H_5(C_{16}H_{31}O_2)_3 = C_{51}H_{98}O_6$, Palmitin,
$C_3H_5(C_{18}H_{35}O_2)_3 = C_{57}H_{110}O_6$, Stearin,
$C_3H_5(C_{18}H_{33}O_2)_3 = C_{57}H_{104}O_6$, Oleïn.

The molecular weights of the constituents of fat are remarkably high.

Butter is another important fat. It consists of the glycerides of butyric acid, $C_4H_8O_2$, caproic acid, $C_6H_{12}O_2$, caprylic acid, $C_8H_{16}O_2$, and capric acid, $C_{10}H_{20}O_2$.

In the vegetable fats, oleïn is predominant, and they are hence usually liquid at ordinary temperatures. The principal ones are:

Olive-oil, which occurs in the fleshy parts of the olive, and is obtained by pressing. It solidifies at a few degrees under 0°.

Cocoanut-oil, obtained from the kernels of the cocoanut. It fuses at 20° and is solid at ordinary temperatures.

Palm-oil, obtained from the *Cocus bulyracea*. Fuses at 27°.

Almond-oil, obtained by pressing almonds. Solidifies at −27°.

None of these oils dry. Among the drying oils are :

Croton-oil, obtained from the seeds of the *Croton tiglium* by pressing.

Castor-oil, obtained by pressing the seeds of the *Ricinus communis*. It is a thick, colorless oil with a sharp taste.

Linseed-oil, obtained from linseed. It is a bright-yellow oil with a peculiar taste and odor. It dries quickly, and hence finds a wide application in the preparation of paints and varnishes.

Hemp-oil, obtained from hemp seed. This oil is also used in paints and varnishes.

Poppy-oil, from the seeds of the poppy. It is a thin, bright-yellow oil, which is chiefly used as food, although occasionally employed in varnishes.

Carbhydrates.

The carbhydrates comprise a class of bodies, all of which belong to the hexane series, and which, as a rule, contain hydrogen and oxygen in the proportions to form water. They are enormously distributed in the vegetable kingdom, and constitute the most important constituent of plant life. They form a group of intimately related bodies, which are either fermentable, or can easily be converted into fermentable compounds.

The carbhydrates are divided into three groups, the first of which has the formula $C_6H_{12}O_6$. The second group may be regarded as the anhydride of the first, as it has the formula $C_{12}H_{22}O_{11}$:

$$2\,C_6H_{22}O_6 - H_2O = C_{12}H_{22}O_{11}.$$

The third group may likewise be considered as a second anhydride of the first, its formula being $C_6H_{10}O_5$, or a multiple thereof.

In the first group, $C_6H_{12}O_6$, are grape-sugar, fruit-sugar, and lactose. The second group, $C_{12}H_{22}O_{11}$, comprises cane-sugar, milk-sugar, melitose, melizitose, and trehalose. The members of the third group, $C_6H_{10}O_5$, are dextrine, gum, glycogen, starch, cellulose, tunicine, and mucilage.

But little is known with certainty concerning the constitution of these bodies. It is evident that the number of isomers in the group is very great. There are five hydrocarbons of the formula C_6H_{14}, and five hexahydric alcohols possible. Among the latter are mannite and dulcite, which we have already noticed. It is not improbable that the compounds of the formula $C_6H_{12}O_6$, may be of an aldehyde nature, as for instance:

$$CH_2(OH)\text{-}CH(OH)\text{-}CH(OH)\text{-}CH(OH)\text{-}CH(OH)\text{-}CHO = C_6H_{12}O_6,$$

and that the compounds of the type, $C_{12}H_{22}O_{11}$, may be formed by the union of two molecules of $C_6H_{12}O_6$, with elimination of a molecule of water, in the same manner that diglycol is formed from glycol.

The carbhydrates which are soluble in water possess the property of bending the plane of polarized light, *i.e.*, they are optically active, a property which we have already had occasion to notice in the case of tartaric acid. They are all indifferent, *i.e.*, neither bases nor acids. On heating, they decompose into a number of substances of lower constitution, leaving carbon. Oxidizing agents convert them into saccharic and mucic acids, and finally into oxalic acid.

Grape-Sugar, *Glucose, Dextrose,* $C_6H_{12}O_6$, is always found together with fruit-sugar in grapes, figs, cherries, and many other sweet fruits, and also in honey. It occurs in small amounts in various animal secretions, particularly in the urine of patients suffering from diabetes. It is formed, together with levulose, by boiling cane-sugar with a dilute acid, and also by the action of saliva, the secretions of the pancreas and intestines, diastase (p. 155), on gum, starch, cellulose, and the glucosides (p. 163).

The grape-sugar is obtained at first as a thick syrup, which gradually crystallizes in cauliflower-like masses, containing one molecule of water. It crystallizes from absolute alcohol, methyl alcohol, or a concentrated aqueous solution kept at a summer temperature, in anhydrous needles. It turns the plane of polarized light to the right. A fresh solution polarizes twice as strongly as one that has stood, or has been boiled a short time.

It loses water when heated to 170°, and is converted into *glucosan,* $C_6H_{10}O_5$. On stronger heating, it loses more water and passes into *caramel,* a brown mixture of various substances which all contain hydrogen and oxygen in the proportions of water. By still stronger heating, it yields methane, carbonic

acid, carbonous oxide, acetic acid, aldehyde, acetone, etc., and leaves a coarsely porous, glittering charcoal.

Grape-sugar unites with bases, but is often decomposed thereby. It also combines with sodium chloride. With acids it forms a species of esters (*glucosides*) which behave like the glycerides.

Dextrose is oxidized easily in the presence of bases. Cupric oxide, when in alkaline solution, is converted into cuprous oxide by it even in the cold, a reaction which is taken advantage of as a means of detecting dextrose, and also for determining it quantitatively in many solutions, *e.g.*, urine, etc.

Cupric sulphate is dissolved in a solution of sodium hydroxide and tartaric acid added. This solution is brought to boiling, and the liquid to be tested is added to it. If a bright red precipitate of Cu_2O is formed in the deep blue solution, the presence of dextrose is indicated.

Nitric acid oxidizes dextrose into saccharic, tartaric, and oxalic acids. Sodium amalgam reduces it to mannite.

Dextrose is easily decomposed by ferments. Yeast produces the alcoholic fermentation, and cheese the butyric and lactic fermentations.

Fermentation. A substance which is decaying often sets up decompositions in other substances which are not subject to change by themselves. The decaying substance is called a *ferment*, and the substance decomposed by the ferment is said to be *fermentable*. The nature of the decomposition of the fermenting substance is determined by the nature of the ferment. Although the ferment sets up the decomposition, its elements do not enter into the products of the fermentation. The ferment may be an easily decomposable organic compound, or an organized body. Nearly all the albuminous substances and the bodies closely related to them have the power of creating fermentation. Among them are

Diastase, a substance which is formed in germinating grains from the decomposition of the gluten.

Synaptase, or *Emulsin*, which occurs in the almond and is very similar to diastase.

The soluble portions of the yeast, the saliva, the secretion of the pancreas, etc.

There is also a number of organized ferments, the principal one of which is

Yeast, the alcoholic ferment. Yeast consists of microscopic plant cells (*Mycoderma cerevisiæ*). They are attached to each other in chains, and grow by budding. To produce the fermentation, it is necessary that the yeast should be alive, for the fermentation ceases as soon as the yeast dies. The sugars are decomposed by yeast, the principal products being alcohol and carbonic acid :

$$C_6H_{12}O_6 = 2\,C_2H_6O + 2\,CO_2.$$

Certain side-products are also formed, the principal of which are highly constituted alcohols, as propyl, isopropyl, isobutyl, and amyl alcohols. Glycerol and succinic acid are also produced.

Among the numerous other organized ferments besides yeast are

The *Lactic Ferment*, which causes one molecule of sugar to break into two molecules of lactic acid :

$$C_6H_{12}O_6 = 2\,C_3H_6O_3,$$

and by continued action converts the lactic acid into butyric acid with evolution of hydrogen :

$$2\,C_3H_6O_3 = C_4H_8O_2 + 2\,CO_2 + 2\,H_2.$$

The mucous ferment, which breaks sugar into lactic acid, mannite, and gum.

Since it appears that each organized ferment produces characteristic fermentation-products, it is possible that the appearance of fusel oils in the fermentation of sugar may be due to the presence of some other organism than the yeast.

Levulose, *Fruit-Sugar*, $C_6H_{12}O_6$,

$$CH_2(OH)$$
$$CH_2(OH)\text{-}CH(OH)\text{-}C(OH)\text{-}CH\text{-}(OH)\text{-}CHO.$$

From dextrose it is distinguished by its turning the plane of polarized light to the left, and by its difficulty in crystallizing. It exists with dextrose in honey and sweet fruits, and is formed together with the former by the inversion of cane-sugar. It is a colorless syrup, which is soluble in all proportions in water and alcohol, and crystallizes from the latter in fine, colorless, silky needles. It is decomposed by ferments, and yields the same products as dextrose.

Lactose, $C_6H_{12}O_6$, is obtained by boiling milk-sugar with dilute acids. It is crystalline, polarizes to the right, is easily soluble in water, insoluble in alcohol, and in its reactions resembles dextrose.

Cane-Sugar, *Saccharose*, $C_{12}H_{22}O_{11}$, probably an ether of dextrose and levulose, viz.,

$$CH_2(OH)\text{-}CH(OH)\text{-}CH(OH)\text{-}CH(OH)\text{-}CH\diagdown$$
$$CH_2(OH)\text{-}CH(OH)\text{-}C(OH)\text{-}CH\text{-}CH\text{-}O\text{-}CH\diagup O$$
$$CH_2(OH)\diagup O\diagdown$$

Cane-sugar is found in the juice of the sugar-cane, the sugar-beet, sugar-maple, maize, sorghum, and in many other plants.

It is made from the juice of the sugar-cane or beet by clearing with lime, evaporating the solution rapidly, and allowing it to crystallize. A crude sugar is thus obtained which is purified by recrystallization (refining)

It crystallizes in limpid, oblique prisms, is easily soluble in water, very difficultly in alcohol. It polarizes to the right. At 160° it fuses to a glass, and when heated for some time at 170°, breaks into dextrose and levulosan.

$$C_{12}H_{22}O_{11} = C_6H_{12}O_6 + C_6H_{10}O_5.$$

At 200° it is converted into *caramel.* Heated higher it decomposes like dextrose into CO_2, CO, C_2H_4O, $C_2H_4O_2$, C_3H_6O, etc., and leaves a coal.

Cane-sugar gives, like dextrose, compounds with alkaline earths and alkalis. Dilute acids convert it into a mixture of dextrose and levulose called *inverted sugar:*

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6.$$

Concentrated sulphuric acid decomposes it completely with carbonization. Alkaline cupric solution reduces it after long boiling, separating cuprous oxide. After having been some time in solution, its polarizing power is less.

It is converted into saccharic acid by gently heating with nitric acid :

$$C_{12}H_{22}O_{11} + 3\,O_2 = 2\,C_6H_{10}O_8 + H_2O\,;$$

but by boiling, into oxalic acid :

$$C_{12}H_{22}O_{11} + 9\,O_2 = 6\,C_2H_2O_4 + 5\,H_2O.$$

It is not directly fermentable, and must be converted into inverted sugar before fermentation can take place.

Milk-Sugar, $C_{12}H_{22}O_{11}$. It is found in the milk of mammals, and together with cane-sugar in the juice of the sapodilla. The milk, after being freed from casein and fat, is evaporated to a syrup, and the milk-sugar crystallizes out in crusts, which are purified by recrystallization.

It forms hard rhombic crystals, which have a sweet taste and are easily soluble in water, but insoluble in alcohol. They contain a molecule of water, which is driven off at 130°. It polarizes to the right.

It is converted by boiling with dilute acids into galactose and another sugar of the formula, $C_6H_{12}O_6$, most probably dextrose. Nitric acid oxidizes it to mucic acid, $C_6H_{10}O_8$, and on boiling, to oxalic acid, $C_2H_2O_4$. Milk-sugar reduces

alkaline cupric solutions like dextrose, but not until boiled. In the milk it goes gradually into the lactic fermentation, owing to the presence of the decomposing casein, but it can also be brought into the alcoholic fermentation.

The Tartars make from mares' milk an intoxicating drink called koumis.

Melitose, $C_{12}H_{22}O_{11}$, is the chief constituent of Australian manna. It crystallizes in fine needles with three molecules of water, two of which it loses at 100°, the third at 130°. It polarizes to the right, and does not reduce alkaline cupric solutions. It is brought into fermentation by yeast, but half of it is transformed thereby into an unfermentable body, *eucalin*, $C_6H_{12}O_6$, which polarizes to the right and reduces alkaline cupric solutions.

Melizitose, $C_{12}H_{22}O_{11} + 2\,H_2O$, is contained in the young shoots of the larch. It polarizes to the right, is not acted on by alkalis, and does not reduce alkaline cupric solutions.

Trehalose, or *mycose*, $C_{12}H_{22}O_{11} + 2\,H_2O$, occurs in the trehala, a kind of Syrian manna which is produced by an insect. It also exists in the ergot of rye and in various fungi. It is easily soluble in water, polarizes to the right, is not acted on by alkalis, does not reduce alkaline cupric solutions, and is converted by acids into a fermentable sugar.

Starch, Amylum, *Amidin, Fecula*, $C_6H_{10}O_5$. Starch is very widely distributed in the vegetable kingdom, and particularly in the seed of the leguminosæ, and in chestnuts, acorns, grain, and potatoes. It consists of microscopic granules of various sizes and forms, which have in their interiors a kernel around which the mass is arranged in concentric layers.

Starch is a fine powder without taste or odor. It is completely insoluble in cold water. It attracts moisture from moist air up to 56 per cent. In water of 72°, the starch granules swell up and partly dissolve, forming a paste which polarizes to the right. Dilute acids change starch first into a gummy soluble substance, *dextrine*, and then into dextrose.

Starch is also converted into dextrine by heating to 160°. Diastase, which occurs in germinating barley, converts starch, when diffused through warm water, into dextrine and maltose.

Concentrated nitric acid dissolves starch, forming a compound which is precipitated by water. It is a nitric ester of starch, and is called *xyloïdin*. Iodine unites with starch, forming an unstable compound which has a very characteristic blue color. By the formation of this color, the slightest traces of starch can be detected.

The most important kinds of starch met with in commerce are :

Maize-starch, potato-starch, arrow-root starch, and *wheat-starch.*

Maltose, $C_{12}H_{22}O_{11}$, or $C_{18}H_{34}O_{17}$. It is formed by the action of diastase on starch at 50–70°, and crystallizes in fine hard needles with one molecule of water. It polarizes strongly to the right, reduces alkaline cupric solutions, and is converted into dextrose by boiling with dilute sulphuric acid. It can be fermented directly. Possibly it may be a compound of dextrine with dextrose, $2\ C_6H_{12}O_6 + C_6H_{10}O_5$.

Among the substances which are closely allied to starch are *inulin, lichenin, paramylum,* and *glycogen.*

Inulin, $C_6H_{10}O_5$, is found in the roots of many plants, particularly in those of *Inula helenium* and the bulbs of the valerian. It is insoluble in cold water, soluble in hot, but without forming a paste. It polarizes to the left, and is not colored blue by iodine. Dilute acids convert it into levulose.

Lichenin, $C_6H_{10}O_5$, occurs in Iceland-moss. It is a transparent, brittle mass, soluble in hot water. It is colored blue by iodine, and is converted into dextrose by dilute acids.

Paramylum, $C_6H_{10}O_5$, occurs in infusoria. It is insoluble in water. In hot water it swells up, but does not form a paste. It can be converted into sugar.

Glycogen, $C_6H_{10}O_5$, is found in the liver shortly after digestion. On the death of the animal it is converted with great rapidity into dextrose by the ferments contained in the liver.

Glycogen is a white powder, dissolving in water to a turbid

solution. Dilute acids and ferments change it easily into dextrose. Iodine colors it wine-red.

Dextrine, *British Gum,* $C_6H_{10}O_5$. It has already been mentioned that starch by heating to 160°, or by continued boiling with dilute acids, or by the action of diastase, is converted into a gummy substance soluble in water, which polarizes very strongly to the right. Dextrine owes its name to the latter property. Dextrine is produced commercially by moistening starch with water containing 2% of nitric acid, drying in the air, and heating to 110°.

Dextrine forms a colorless amorphous mass which does not reduce alkaline cupric solutions, is not colored blue by iodine, and yields oxalic acid on oxidation. Dilute sulphuric acid, or diastase, converts it into dextrose.

Gums. A large number of resinous substances are included under the name of gums. With water they swell up, or dissolve, forming thick, sticky masses. Alcohol precipitates them from their aqueous solutions. They polarize either right or left, according to their derivation. *Gum-arabic* consists of the calcium salt of *arabic acid,* $C_{12}H_{22}O_{11}$.

Cellulose, Plant-Fiber, $C_6H_{10}O_5$. The walls of plant-cells and the skeleton of plants consist of cellulose. It may be obtained in the pure state from cotton or linen, and is a white translucent mass, insoluble in water. It is soluble in an ammoniacal solution of basic cupric carbonate, and is precipitated by acids, being redissolved, however, by an excess. It is not colored blue by iodine. With concentrated sulphuric acid, it swells up and gradually dissolves, being precipitated in white flocks by water. The body thus obtained is an altered cellulose and is colored blue by iodine. It is called *amyloid.*

If unsized paper, which is almost pure cellulose, is allowed to remain a few seconds in sulphuric acid diluted with half its volume of water, and then well washed with water, it is

converted into a substance like parchment which is called "parchment paper." The surface of the paper is converted into amyloid by this operation.

Cellulose is converted into oxalic acid by oxidation with nitric acid. If, however, cellulose (cotton) is allowed to remain in a mixture of concentrated sulphuric (3 parts) and nitric acids (1 part), it is converted, without being dissolved, into *nitro-cellulose, pyroxylin,* or *gun-cotton:*

$$C_5H_7(NO_3)_3O_5.$$

Gun-cotton detonates when brought in contact with a red-hot body. It is an extremely explosive body. It is insoluble in water, alcohol, and ether. If the above relations between the sulphuric and nitric acids are altered, the nitrition does not go so far, and a substance is produced which is soluble in a mixture of alcohol and ether. It is called *collodion,* and is extensively used in photography.

These so-called nitro-compounds, as nitroglycerol and nitrocellulose, are really nitric esters. The difference between the nitric esters and the true nitro-compounds has already been explained under the methyl compounds. We shall have occasion to refer to this difference when we come to consider the aromatic series.

Gun-cotton and collodion are converted back into cellulose by reducing agents.

In the mantles of certain mollusks (*ascidia*), a substance is found which resembles cellulose very much, and is perhaps identical with it. It is called *tunicin.*

Vegetable Mucus, or *Mucilage,* is found in many plants, particularly in the roots of the althæa, the linseed, quince-seeds, etc. In cold water, it swells up to a slimy jelly, which is dissolved by hot water. Alcohol precipitates it. There are various kinds of vegetable mucus, which are distinguished by their derivation, and differ somewhat in composition, but they all give dextrose on boiling with dilute sulphuric acid.

The *pectine substances*, which occur in beets and in fleshy fruits, are very similar to vegetable mucus.

We shall mention finally several bodies which are fermentable and very closely allied to the carbhydrates.

Sorbin, $C_6H_{12}O_6$, occurs in the berries of the mountain ash.

It crystallizes in rhombic octahedrons, tastes as sweet as cane-sugar, is easily soluble in water, and less soluble in alcohol. It reduces alkaline cupric solutions, and polarizes to the left. Yeast does not bring it into fermentation, nor do dilute acids convert it into dextrose. On heating, it loses water and decomposes

Inosite, $C_6H_{12}O_6$, exists in the flesh of the muscles, the muscular substance of the lungs, in the brain, and in unripe leguminosæ. It forms cauliflower-like, crystalline aggregates, containing two molecules of water, which it loses at 100°. It cannot be brought into the alcoholic fermentation, nor do dilute acids convert it into a fermentable sugar. Decomposing animal matters, however, produce the lactic fermentation in it. It is optically inactive.

Arabinose, $C_6H_{12}O_6$, is formed, together with a fermentable sugar, by boiling gum-arabic with dilute sulphuric acid. It crystallizes in large, beautiful prisms, fusing at 160°, and easily soluble in water. It has a very sweet taste, reduces alkaline cupric solutions, polarizes to the right, and cannot be brought into fermentation.

There stands in intimate relation to the carbhydrates a large class of compounds which are very widely distributed in the vegetable kingdom. They are compounds of a sugar, usually dextrose, with one or more other substances, and belong to the class of ethers. They are called *glucosides*. By boiling with dilute acids, or alkalis, or by ferments, they are decomposed into the sugar and the other constituent.

The substance in combination with the sugar belongs almost always to a group of bodies which we have not yet considered, and which are gener-

ally treated of apart as a class by themselves, because their carbon atoms have a peculiar mutual binding. We shall, therefore, take up the consideration of the glucosides after the description of this other class of compounds which we call the aromatic series.

Uric Acid and its Derivatives.

Uric acid belongs properly to the propane group, but it was not considered under that series because of its complicated constitution, and since it was not deemed advisable to separate it from many of its derivatives which belong to the ethane series.

Uric acid occurs free and in the form of salts in the urine of all vertebrate animals, in smaller amounts in the urine of mammalia, and in very small amounts in that of the herbivora, it being here replaced by hippuric acid. It exists in large amounts in the secretions of birds, amphibians, and many insects. Occasionally it is deposited in the bladder and forms concretions. It is made from the excrements of snakes, which consist almost entirely of uric acid.

Uric Acid, $C_5H_4N_4O_3$, is a white, crystalline powder, very difficultly soluble in hot water, and almost insoluble in cold water. It forms two series of salts with bases, of which the acid ammonium and acid potassium salts are the most important. The former is the material from which the acid is made; the latter, owing to its difficult solubility, is used in purifying it. The lithium salt, which is the most easily soluble in water, is also worthy of notice.

Uric acid is decomposed by heat, evolving ammonium cyanate and carbonate, and leaving a nitrogenous coal. On heating with iodohydric acid, it takes up water and breaks into carbonic acid, ammonia, and glycocoll:

$$C_5H_4N_4O_3 + 5\,H_2O = 3\,CO_2 + 3\,NH_3 + \underset{\text{Glycocoll}}{C_2H_5NO_2}.$$

It yields a number of products on oxidation, the nature of which depends on whether the oxidation is performed in an acid or an alkaline solution.

1) By the moderate action of nitric acid, it is decomposed into urea and *alloxan*, $C_4H_2N_2O_4$:

$$\underset{}{C_5H_4N_4O_3} + H_2O + O = \underset{\text{Urea}}{CH_4N_2O} + \underset{\text{Alloxan}}{C_4H_2N_2O_4}.$$

By further action, the alloxan is converted into *parabanic acid*, $C_3H_2N_2O_3$, and carbonic acid :

$$\underset{\text{Alloxan}}{C_4N_2H_2O_4} + O = \underset{\text{Parabanic acid}}{C_3H_2N_2O_3} + CO_2,$$

while, at the same time, the alloxan takes up the elements of water, forming *alloxanic acid*, $C_4H_4N_2O_5$:

$$\underset{\text{Alloxan}}{C_4H_2N_2O_4} + H_2O = \underset{\text{Alloxanic acid}}{C_4H_4N_2O_5},$$

and the parabanic acid yields, at the same time, *oxaluric acid*, $C_3H_4N_2O_4$:

$$\underset{\text{Parabanic acid}}{C_3H_2N_2O_3} + H_2O = \underset{\text{Oxaluric acid}}{C_3H_4N_2O_4}.$$

Alloxanic and oxaluric acids take up the elements of water on boiling, and break into urea and *mesoxalic acid*, $C_3H_2O_5$, or oxalic acid, $C_2H_2O_4$:

$$\underset{\text{Alloxanic acid}}{C_4H_4N_2O_5} + H_2O = \underset{\text{Urea}}{CH_4N_2O} + \underset{\text{Mesoxalic acid}}{C_3H_2O_5}$$

$$\underset{\text{Oxaluric acid}}{C_3H_4N_2O_4} + H_2O = \underset{\text{Urea}}{CH_4N_2O} + \underset{\text{Oxalic acid}}{C_2H_2O_4}.$$

2) A solution of uric acid in potassa is gradually oxidized to *uroxanic acid*, $C_5H_6N_4O_6$:

$$C_5H_4N_4O_3 + 2\,H_2O + O = C_5H_6N_4O_6.$$

Uric acid is oxidized by potassium permanganate into *allantoïn*, $C_4H_6N_4O_3$:

$$C_5H_4N_4O_3 + H_2O + O = C_4H_6N_4O_3 + CO_2,$$

which by further oxidation passes into *allantoxanic acid*, $C_4H_3N_3O_4$:

$$C_4H_6N_4O_3 + O = C_4H_3N_3O_4 + NH_3.$$

Uric acid may be detected in the smallest amounts by moistening with nitric acid, drying, and moistening the onion-red residue with ammonia. A superb purple-red color is obtained. (*Murexide.*)

The constitution of urea, as we have seen, is :

$$CO\begin{cases}NH_2\\NH_2\end{cases}\quad\text{(Carbamide),}$$

of oxalic acid, $\begin{matrix}COOH\\|\\COOH\end{matrix}$, and of mesoxalic acid, $\begin{matrix}COOH\\|\\CO\\|\\COOH\end{matrix}$

If we imagine an H of the amido-group of urea to be replaced by the rest of oxalic acid (oxalic acid minus OH) we have :

$$CO\begin{cases}NH\text{-}CO\text{-}COOH,\\NH_2\end{cases}\quad\text{or } C_3H_4N_2O_4,$$

or oxaluric acid. If the replacement takes place with the rest of mesoxalic acid, we have :

$$CO\begin{cases}NH\text{-}CO\text{-}CO\text{-}COOH,\\NH_2\end{cases}\quad\text{or } C_4H_4N_2O_5,$$

or *alloxanic acid.* Alloxanic acid, however, is formed from alloxan, which contains one H_2O less. Alloxan is, therefore, a more intimate mutual combination of the atomic groups :

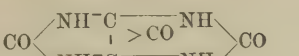
$$CO\begin{cases}NH\text{-}CO\\NH\text{-}CO\end{cases}CO,$$

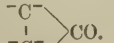
or urea, in which an H of each of the two amido-groups is replaced by the di-valent rest of mesoxalic acid. Parabanic acid is :

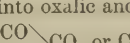
$$CO\begin{cases}NH\text{-}CO\\NH\text{-}\begin{matrix}|\\CO\end{matrix}\end{cases},$$

or urea in which an H of each of the two amido-groups is replaced by the di-valent rest of oxalic acid. In the case of uric acid, its decomposition into urea and alloxan must be taken into account. It contains, therefore, a urea rest, but since the alloxan is formed by oxidation, it must contain an atom of oxygen less than the sum of the atoms of urea and alloxan less water.

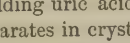
Uric acid may perhaps be considered as:



i.e., two urea rests bound together by the group  It is easily to be understood that the group C_3O is converted into mesoxalic acid by oxidation, and finally into oxalic and carbonic acids.

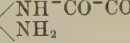
Alloxan,  , or $C_4H_2N_2O_4$.

It is produced by adding uric acid in portions to concentrated nitric acid. The alloxan separates in crystals. It is soluble in water, has an offensive odor, and colors the skin red. Dilute alkalis convert it into

Alloxanic acid,  , or $C_4H_4N_2O_5$, which crystallizes in needles and forms two series of salts. It is converted by reducing agents (zinc and chlorhydric acid) into *alloxantine*, $C_8H_4N_4O_7$:

$$2\,C_4H_4N_2O_5 + H_2 = C_8H_4N_4O_7 + {}_3H_2O,$$

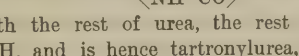
which by further reduction passes into

Dialuric acid, $C_4H_4N_2O_4$, or  . Dialuric acid contains, together with the rest of urea, the rest of tartronic acid, $COOH^-CH(OH)^-COOH$, and is hence tartronylurea, just as alloxan is mesoxylurea, and parabanic acid, oxalurea.

Dialuric acid crystallizes in light yellow prisms, and is a monobasic acid. On mixing dialuric acid and a solution of alloxan, *alloxantine* is formed :

$$\underset{\text{Dialuric acid}}{C_4H_4N_2O_4} + \underset{\text{Alloxan}}{C_4H_2N_2O_4} = C_8H_4N_4O_7 + H_2O.$$

The constitution of alloxantine is, therefore,



Alloxantine, on boiling with a solution of ammonium chloride, breaks into alloxan and dialuramide :

$$\underset{\text{Alloxantine}}{C_8H_4N_4O_7} + NH_4Cl = \underset{\text{Alloxan}}{C_4H_2N_2O_4} + \underset{\text{Dialuramide}}{C_4H_5N_3O_3} + HCl.$$

Dialuramide, or *uramile*, is also formed by the reduction of nitro- or nitrosobarbituric acid, and has the constitution

$$CO\langle\begin{matrix}NH\text{-}CO\\NH\text{-}CO\end{matrix}\rangle CH(NH_2).$$

It is insoluble in water and soluble in ammonia. On boiling with potassium cyanate, it forms a potassium salt isomeric with the uric acid salt, *potassium pseudo-urate*.

Pseudo-uric acid is probably

$$CO\langle\begin{matrix}NH\text{-}CO\\NH\text{-}CO\end{matrix}\rangle CH\text{-}NH\text{-}CN.$$

By the oxidation of dialuramide, *murexide*, the ammonium salt of purpuric acid, is obtained.

Purpuric acid stands to dialuramide in the same relation as alloxantine to dialuric acid. It is, therefore, *alloxantinimide:*

$$\underset{\text{Dialuramide}}{2\,C_4H_5N_3O_3} + O = \underset{\text{Murexide}}{C_8H_5N_6O_6} + H_2O.$$

$$\underset{\text{Murexide}}{C_8H_5N_6O_6} = \underset{\text{Purpuric acid}}{C_8H_5N_5O_5} \cdot NH_3.$$

Murexide forms golden-greenish leaflets which are difficultly soluble in water, but which impart to it an intense purple color. It is soluble in potassa with an indigo-blue color which is destroyed on boiling, with the evolution of ammonia. Acids decompose it on boiling into alloxan and dialuramide.

Murexide is used as a red dye for fabrics.

On heating dialuric acid with glycerol, we obtain

Hydurilic acid, $C_8H_6N_4O_6$: $2\,C_4H_4N_2O_4 = C_8H_6N_4O_6 + H_2O + O$,

$$CO\langle\begin{matrix}NH\text{-}CO\\NH\text{-}CO\end{matrix}\rangle CH\text{-}CH\langle\begin{matrix}CO\text{-}NH\\CO\text{-}NH\end{matrix}\rangle CO$$

which crystallizes in small prisms containing $2\,H_2O$, and difficultly soluble in water and alcohol. From this is obtained

Barbituric acid, $C_4H_4N_2O_3$, which crystallizes in large prisms. Bromine converts it into *dibrombarbituric acid*, $C_4H_2Br_2N_2O_3$, fuming nitric acid into *nitrobarbituric acid*, or *dilituric acid*, $C_4H_3(NO_2)NO_3$. Nitrous acid transforms it into *nitrosobarbituric acid*, or *violuric acid*, $C_4H_3(NO)N_2O_3$.

Barbituric acid, $CO\langle\begin{matrix}NH\text{-}CO\\NH\text{-}CO\end{matrix}\rangle CH_2$, is malonylurea, and on boiling with dilute potassa falls into malonic acid and urea:

$$CO\langle\begin{matrix}NH\text{-}CO\\NH\text{-}CO\end{matrix}\rangle CH_2 + 2\,H_2O = CO\langle\begin{matrix}NH_2\\NH_2\end{matrix}\rangle + \begin{matrix}COOH\\|\\CH_2\\|\\COOH\end{matrix}.$$

Thus far we have considered

Malonylurea, or barbituric acid, $CO\langle\begin{matrix}NH\text{-}CO\\NH\text{-}CO\end{matrix}\rangle CH_2$,

Tartronylurea, or dialuric acid, $CO\langle\begin{matrix}NH\text{-}CO\\NH\text{-}CO\end{matrix}\rangle CH(OH)$,

Mesoxylurea, or alloxan, $CO\langle\begin{matrix}NH\text{-}CO\\NH\text{-}CO\end{matrix}\rangle CO$.

Parabanic acid, oxalylurea, $CO\langle\begin{matrix}NH\text{-}CO\\|\\NH\text{-}CO\end{matrix}$, or $C_3H_2N_2O_3$, is obtained by allowing a solution of urea in nitric acid to evaporate. It is soluble in water. On boiling with ammonia it yields

Oxaluric acid, $CO\langle\begin{matrix}NH\text{-}CO\text{-}COOH\\NH_2\end{matrix}$, or $C_3H_4N_2O_4$, which is a monobasic acid difficultly soluble in water. On boiling with alkalis it breaks into urea and oxalic acid :

$$CO\langle\begin{matrix}NH\text{-}CO\text{-}COOH\\NH_2\end{matrix} + H_2O = CO\langle\begin{matrix}NH_2\\NH_2\end{matrix}\rangle + \begin{matrix}COOH\\|\\COOH\end{matrix}.$$

By the action of reducing agents on parabanic acid, *oxalantine,* $C_6H_4N_4O_5$, is obtained, which corresponds to alloxantine, and which by further reduction passes into

Allanturic acid, $C_3H_4N_2O_3$, or $CO\langle\begin{matrix}NH\text{-}CO\\|\\NH\text{-}CH(OH)\end{matrix}$, or glyoxylurea.

Allied to this compound is

Hydantoïne, or *glycolylurea,* $C_3H_4N_2O_2$, or $CO\langle\begin{matrix}NH\text{-}CO\\|\\NH\text{-}CH_2\end{matrix}$. This body is obtained by the digestion of *allantoïne,* $C_4H_6N_4O_3$, a compound occurring in the urine of calves and of the fœtal calf, with iodohydric acid :

$$\underset{\text{Allantoïne}}{C_4H_6N_4O_3} + 2\,HI = \underset{\text{Urea}}{CH_4N_2O} + \underset{\text{Hydantoïne}}{C_3H_4N_2O_2} + I_2.$$

Allantoïne is formed by the oxidation of uric acid in alkaline solution, and also by heating glyoxylic acid ($CHO\text{-}COOH$) with urea. It crystallizes in glittering prisms, which are difficultly soluble in cold water and are decomposed by boiling with alkalis.

Hydantoïne forms needles fusing at 206°. On boiling with baryta water they give

Hydantoic acid, $C_3H_6NO_3$, or $CO_2\begin{cases}NH_2\\NH\text{-}CH_2\text{-}COOH\end{cases}$, an acid crystallizing in large prisms. It can be produced by heating glycocoll with urea.

We have thus three bodies which can be derived from each other by oxidation (or inversely by reduction):

Glycolylurea, or hydantoïne, $CO\begin{cases}NH\text{-}CO\\NH\text{-}CH_2\end{cases}$

Glyoxylurea, or allanturic acid, $CO\begin{cases}NH\text{-}CO\\NH\text{-}CH(OH)\end{cases}$

Oxalylurea, or parabanic acid, $CO\begin{cases}NH\text{-}CO\\NH\text{-}CO.\end{cases}$

To conclude, we shall take up several bodies and their decomposition-products, which occur in the animal organism.

Xanthine, $C_5H_4N_4O_2$, is a normal constituent of many animal tissues. It is an amorphous powder, very difficultly soluble in water. It combines with both acids and bases.

Sarcine, or *Hypoxanthine*, $C_5H_4N_4O$, occurs in the juice of the muscles, in the spleen, liver, kidneys, brain, etc. It is a crystalline powder, difficultly soluble in cold water, more easily in hot. It possesses basic properties, and decomposes at 150°. Its ammoniacal solution gives a precipitate with silver nitrate:

$$C_5H_2Ag_2N_4O + H_2O.$$

The flesh of muscles contains, besides sarcine,

Carnine, $C_7H_8N_4O_3 + H_2O$, which is a colorless powder, difficultly soluble in water. Nitric acid converts it into hypoxanthine.

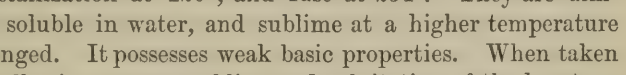
If the above compounds are compared with uric acid, it will be noticed that they form a series, the members of which increase by an atom of oxygen. They are similar in their chemical relations, and probably have an analogous constitution.

Sarcine.....$C_5H_4N_4O$
Xanthine.....$C_5H_4N_4O_2$
Uric acid .....$C_5H_4N_4O_3$

Theobromine, $C_7H_8N_4O_2$, and *Caffeïne*, $C_8H_{10}N_4O_2$, are homologous with xanthine, and have a similar constitution. Theobromine exists in the cocoa-nuts. It is difficultly soluble in water, and forms crystalline salts with acids. *Caffeïne*, *Theïne*, or *Methyltheobromine*, $C_8H_{10}N_4O_2 + H_2O$, is contained in coffee and tea. It forms fine needles, which lose their water of crystallization at 120°, and fuse at 234°. They are difficultly soluble in water, and sublime at a higher temperature unchanged. It possesses weak basic properties. When taken internally, it causes trembling and palpitation of the heart.

Theobromine is dimethylxanthine, $C_7H_8N_4O_2 = C_5H_2(CH_3)_2N_4O_2$; and caffeïne is trimethylxanthine, $C_8H_{10}N_4O_2 = C_5H(CH_3)_3N_4O_2$.

Their constitution is probably:



Guanine, creatine, and creatinine are closely related to this group.

Guanine, $C_5H_5N_5O$, we may imagine to be derived from xanthine by the replacement of an O by NH. It is converted into xanthine by the action of nitrous acid. It is the chief constituent of the excrement of spiders, and occurs in small amounts in guano. It is a white powder which unites both with acids and bases. It is decomposed by oxidation into guanidine, parabanic acid, and carbonic acid:

$$C_5H_5N_5O + 3\,O + H_2O = \underset{\text{Guanidine}}{CH_5N_3} + \underset{\text{Parabanic acid}}{C_3H_2N_2O_3} + CO_2.$$

While the rest of urea, $CO\langle\begin{smallmatrix}NH-\\NH-\end{smallmatrix}$, is common to the group of sarcine, xanthine, and uric acid, the rest of the guanidine molecule, $C(NH)\langle\begin{smallmatrix}NH-\\NH-\end{smallmatrix}$,

is characteristic of guanine. This rest, $C(NH)\begin{matrix}NH^-\\NH^-\end{matrix}$, is also common to the following substances :

Creatine, $C\begin{matrix}NH_2\\=NH\\N(CH_3)^-CH_2COOH\end{matrix}$, or $C_4H_9N_3O_2$.

Occurs in the juice of the muscles of herbivora. It crystallizes in limpid, rhombic prisms containing one molecule of H_2O, which is driven off at 100°. They possess a bitter, salty taste, are difficultly soluble in cold water, quite easily in hot, and possess weak basic properties.

By heating creatine with dilute acids the elements of water split out, forming

Creatinine, $C\begin{matrix}NH\\\text{———}\\N(CH_3)^-CH_2\end{matrix}\begin{matrix}NH\\\rangle CO\end{matrix}$, or $C_5H_7N_3O$.

Creatinine occurs in the urine and muscles of men, horses, dogs, etc. It crystallizes in quite soluble rhombic prisms, which possess an alkaline reaction and strong basic properties. It forms a characteristic compound with zinc chloride, $(C_4H_7N_3O)_2ZnCl_2$.

Creatine, on boiling with dilute alkalis, is resolved into *methylglycocoll* and urea, the latter breaking up into carbonic acid and ammonia :

$$C_4H_9N_3O_2 + H_2O = C_3H_7NO_2 + CH_4N_2O.$$

Methylglycocoll, or *Sarcosine*, $\begin{matrix}CH_2^-NH(CH_3)\\|\\COOH\end{matrix}$, or $C_3H_7NO_2$, is formed from monochloracetic acid and methylamine :

$$\begin{matrix}CH_2Cl\\|\\COOH\end{matrix} + CH_3NH_2 = \begin{matrix}CH_2^-NH(CH_3)\\|\\COOH\end{matrix} + HCl.$$

It forms rhombic prisms which are soluble in water, and volatilize without decomposition. It has weak basic properties.

Creatine is converted by oxidizing agents into

Methyluramine, methylguanidine, $C_2H_7N_3$, or $C{=}\begin{smallmatrix}NH_2\\NH\\NH(CH_3)\end{smallmatrix}$, a deliquescent, strongly basic substance.

Standing between methyluramine and creatine is

Glycocyamine, $C_3H_7N_3O_2$, or $C{=}\begin{smallmatrix}NH_2\\NH\\NH\text{-}CH_2\text{-}COOH\end{smallmatrix}$. It is obtained from glycocoll and cyanamide, and is a glycocoll in which an H is replaced by the glycocoll-rest. It is a crystalline, strongly basic body, difficultly soluble in water. The hydrochloride of glycocyamine, on heating to 160°, is converted into the salt of glycocyamidine, $C_3H_5N_3O$, or $(NH)\begin{smallmatrix}NH\text{-}CH_2\\NH\text{-}CO\end{smallmatrix}$.

The most important of the above compounds is creatine, which is a methylguanidine in which an H of the NH_2 is replaced by a glycollic acid rest.

Guanidine, $C{=}\begin{smallmatrix}NH\\NH_2\\NH_2\end{smallmatrix}$

Methylguanidine, $C{=}\begin{smallmatrix}NH\\NH_2\\NH(CH_3)\end{smallmatrix}$

Creatine, $C{=}\begin{smallmatrix}NH\\NH_2\\N(CH_3)\text{-}CH_2\text{-}COOH\end{smallmatrix}$

Glycollic acid, $CH_2(OH)\text{-}COOH$.

Retrospect.

THE large number of bodies which we have thus far met with, can, as we have seen, be traced back to a few compounds, the principal characteristics of which appear in their representatives in all the carbon series. We have repeatedly noticed that the alcohols, aldehydes, acids, chlorides, etc., always exhibit characteristic reactions.

We shall now consider the chief classes arranged, not according to the carbon series, but according to the nature of the substitution.

We meet at first those compounds which consist only of carbon and hydrogen, the *hydrocarbons*, and of these the saturated hydrocarbons come first.

$CH_4 = CH_4$ Methane,

$C_2H_6 = CH_3{-}CH_3$ Ethane,

$C_3H_8 = CH_3{-}CH_2{-}CH_3$ Propane,

$C_4H_{10} =$ 1) $CH_3{-}CH_2{-}CH_2{-}CH_3$; 2) $CH_3{-}CH(CH_3){-}CH_3$ Butane (2 isomers),

$C_5H_{12} =$ 1) $CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_3$; 2) $CH_3{-}CH_2{-}CH(CH_3){-}CH_3$; 3) $CH_3{-}C(CH_3)_2{-}CH_3$ Pentane (3 isomers),

$$C_6H_{14} = \begin{cases} 1)\ CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 \\ 2)\ CH_3\text{-}CH_2\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_3 \\ 3)\ CH_3\text{-}CH(CH_3)\text{-}CH(CH_3)\text{-}CH_3 \\ 4)\ CH_3\text{-}CH_2\text{-}C(CH_3)_2\text{-}CH_2\text{-}CH_3 \\ 5)\ CH_3\text{-}CH_2\text{-}C(CH_3)_3 \end{cases} \text{Hexane (5 isomers),}$$

We shall stop with hexane, as the number of isomers increases extraordinarily in the higher series, according to the law of permutations. Of heptane, C_7H_{16}, there are 9 isomers; of octane, C_8H_{18}, 35; of nonane, C_9H_{20}, 155, etc. Only a few of these isomers are known, but new ones are being continually obtained.

These hydrocarbons are formed by the decomposition of coal, the first member, methane, being contained in illuminating gas, while the others exist in petroleum. They can be produced artificially in the following manner:

1) By the dry distillation of a salt of a monobasic acid of the next higher series with an alkali:

$$\underset{\text{Sodium acetate}}{CH_3\text{-}COONa} + NaHO = CH_4 + Na_2CO_3$$

$$\underset{\text{Sodium propionate}}{C_2H_5\text{-}COONa} + NaHO = C_2H_6 + Na_2CO_3.$$

2) By the electrolysis of the corresponding monobasic acid:

$$2\,CH_3\text{-}COOH = CH_3\text{-}CH_3 + 2\,CO_2 + H_2.$$

3) By treatment of the zinc compound with water:

$$(CH_3)_2Zn + 2\,H_2O = 2\,CH_4 + Zn(OH)_2.$$

4) By treatment of the iodo-compound with sodium, a hydrocarbon of a higher series being formed :

$$\begin{matrix} CH_3I \\ CH_3I \end{matrix} + Na_2 = \begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} + 2\,NaI.$$

The lower members of this series, up to butane, are gaseous at ordinary temperatures. Pentane is a liquid boiling at a low temperature. The boiling points of the higher members, as for instance of those which are contained in petroleum, rise above 360°. The boiling points of the different isomers of a carbon series are, of course, different.

The saturated hydrocarbons are characterized by the difficulty with which they are attacked by reagents, *i.e.*, yield substitution-products. Chlorine reacts with a few in the sunlight, but with the majority the reaction takes place only at a high temperature :

$$C_8H_{18} + Cl_2 = C_8H_{17}Cl + HCl.$$

From their stability as regards substituting agents, these hydrocarbons are called *paraffines* (from para affinis, without affinity). Their general formula is C_nH_{2n+2}. Hydrocarbons (and all organic compounds) having a similar constitution, and which are derived from each other by the replacement of an H by a CH_3, are called *homologous*. Thus all saturated hydrocarbons are homologous with methane, but pentane No. 3, and butane No. 1 are not homologous. Those hydrocarbons in which each carbon atom is bound with at most two other carbon atoms, so that each carbon atom consequently binds at least two hydrogen atoms, are called *normal*. In the series just given, the normal hydrocarbons are placed first.

The general rule for the hydrocarbons of the series C_nH_{2n+2}, is that each carbon atom is bound by only one bond to another carbon atom.

Unsaturated Hydrocarbons.

The carbon atoms of the unsaturated hydrocarbons are bound together by more than one bond. The simplest case is of two carbon atoms bound together each by two bonds, while the other carbons are bound as in the saturated hydrocarbons. In this manner, compounds of the type C_nH_{2n} are formed.

C_2H_4 $= CH_2{=}CH_2$ — Ethylene,

C_3H_6 $=$ 1) $CH_3{-}CH{=}CH_2$ — Propylene,

C_4H_8 $=$ 1) $CH_3{-}CH_2{-}CH{=}CH_2$

2) $CH_3{-}CH{=}CH{-}CH_3$ — Butylene,

3) $CH_3{-}C(CH_3){=}CH_2$

C_5H_{10} $=$ 1) $CH_3{-}CH_2{-}CH_2{-}CH{=}CH_2$

2) $CH_3{-}CH_2{-}CH{=}CH{-}CH_3$

3) $CH_3{-}CH{=}C(CH_3){-}CH_3$ — Amylene,

4) $CH_3{-}CH_2{-}C(CH_3){=}CH_2$ — (Pentylene).

These hydrocarbons are formed by the decomposition of many organic compounds at a high temperature; by the action of dehydrating agents (conc. H_2SO_4, P_2O_5, etc.) on monohydric alcohols; and by treatment of their chlorides, bromides, or iodides, with potassium hydroxide:

$$C_3H_7I + KOH = C_3H_6 + KI + H_2O.$$

The secondary and tertiary alcohols and their halogen derivatives break very easily into unsaturated hydrocarbons:

$$\underset{\text{Ethyl alcohol}}{CH_3{-}CH_2OH} - H_2O = \underset{\text{Ethylene}}{CH_2{=}CH_2}.$$

The first members of this series, as ethylene, propylene,

butylene, etc., are gaseous at ordinary temperatures. The higher ones are liquids or solids.

They unite easily with the halogens:

$$CH_2{=}CH_2 + Br_2 = \underset{\text{Ethylene bromide}}{CH_2Br{-}CH_2Br},$$

and with the halogen-hydric acids:

$$CH_2{=}CH_2 + HI = \underset{\text{Ethyl iodide}}{CH_3{-}CH_2I},$$

also with sulphuric acid:

$$CH_2{=}CH_2 + H_2SO_4 = \underset{\text{Ethylsulphuric acid}}{CH_3{-}CH_2 . HSO_4},$$

forming derivatives of the saturated hydrocarbons. The double binding is hence easily dissolved. They are also easily polymerized by substances having an attraction for water (sulphuric acid, etc.). They are called *olefines*.

There are, however, unsaturated hydrocarbons which contain carbon atoms bound with more than two bonds, or in which there are more than two carbon atoms bound by two bonds.

1) C_nH_{2n-2} series.

$C_2H_2 =$ $CH{\equiv}CH$ — Acetylene,

$C_3H_4 =$ 1) $CH{\equiv}C{-}CH_3$, 2) $CH_2{=}C{=}CH_2$ — Allylene, or propylene,

$C_4H_6 =$ 1) $CH{\equiv}C{-}CH_2{-}CH_3$, 2) $CH_3{-}C{\equiv}C{-}CH_3$, 3) $CH_2{=}C{=}CH{-}CH_2$, 4) $CH_2{=}CH{-}CH{=}CH_2$ — Crotonylene, or butylene,

C_5H_8, Pentylene, C_6H_{10}, Hexylene, etc.

The hydrocarbons of the series, C_nH_{2n-2}, are formed by the action of alcoholic potassa on the compounds of the $C_nH_{2n}Br_2$ series:

$$CH_2Br{-}CH_2Br + 2\,KHO = CH{\equiv}CH + 2\,KBr + 2\,H_2O,$$
$$\text{or } C_2H_4Br_2 - 2\,HBr = C_2H_2.$$

These hydrocarbons unite easily with two and four atoms of a halogen :

$$C_3H_4 + Cl_2 = C_2H_4Cl_2$$
$$C_3H_4 + Cl_4 = C_3H_4Cl_4.$$

2) C_nH_{2n-4} series.

Only the higher members are known : C_5H_6, valylene, a large number of the compounds of the formula $C_{10}H_{16}$ (the terpenes), and the majority of the essential oils, of which the more important will be considered later on, belong to this series. It is easy to see that the number of isomers of the composition, $C_{10}H_{16}$, will be large.

3) C_nH_{2n-6} series. The remarkably large number, and the great importance of the compounds of this particular class (the aromatic series), have led chemists from an early date to treat them as a separate class. We shall soon have an opportunity of studying them. The hydrocarbons which contain still less hydrogen will also be taken up later on.

The substances called *petroleum* and *paraffine*, which are met with in commerce, are mixtures of numerous hydrocarbons belonging to the C_nH_{2n+2} and C_nH_{2n} series. As the hydrocarbons of the lower series (CH_4, C_2H_6, C_3H_8, etc.), are gaseous at ordinary temperature, while those of the higher series (C_6H_{14}, C_6H_{12}, C_7H_{16}, etc.), are liquid, and the still more complicated ones ($C_{20}H_{42}$, etc.), are solid, the difference between petroleum and paraffine lies chiefly in the former consisting for the greater part of hydrocarbons under C_{20}, while paraffine is composed chiefly of those from C_{20} to C_{27}.

Petroleum occurs in many places, but particularly in the United States. It is formed by the slow decomposition of organized bodies (plants and animals). Crude petroleum, as it issues from the earth, contains also the lower hydrocarbons, the greater part of which are evolved in a gaseous state, although a part of them remain in solution. On account of the gaseous and low boiling hydrocarbons which it contains, petroleum begins to boil at a low temperature, and as it ignites very easily, has given rise to many accidents. It has, therefore, to be rectified, *i.e.*, distilled. The portions going over between 150° and 200° constitute the petroleum of commerce (kerosene).

The portion distilling under 150° is also utilized. That which goes over under 100° is known as *petroleum-ether*, *cymogen*, *rigolene*, etc., while that between 100° and 150° constitues the article known as *benzine*, or *ligroine*, which is used as a solvent for fats, resins, caoutchouc, etc., and for making gas. On account of its inflammability, it has to be handled with great care.

Petroleum also contains paraffine, *i.e.*, the liquid hydrocarbons hold solid ones in solution. Paraffine is also obtained by the dry distillation of wood, peat, and bituminous shales. It is a white, fatty substance resembling wax. It fuses at about 40° and boils over 300°.

Halogen Derivatives of the Hydrocarbons.

Both the saturated and unsaturated hydrocarbons yield substitution-derivatives in which one or more atoms of hydrogen are replaced by chlorine, bromine, or iodine. The number of isomeric derivatives is greater than the number of the hydrocarbons. Ethane, C_2H_6, for instance, yields two isomeric dichlor-derivatives, $CH_2Cl\text{-}CH_2Cl$, ethylene chloride, and $CH_3\text{-}CHCl_2$, ethylidene chloride. Butane, C_3H_8, or $CH_3\text{-}CH_2\text{-}CH_3$, yields two monochlor-derivatives, $CH_3\text{-}CH_2\text{-}CH_2Cl$ and $CH_3\text{-}CHCl\text{-}CH_3$.

The monochlorides, bromides, and iodides are generally made from the monohydric alcohols, either by digesting with gaseous chlorhydric acid, or by treating them with phosphorus chloride, bromide, or iodide :

$$C_2H_5(OH) + HCl = C_2H_5Cl + H_2O,$$
$$3\,C_2H_5(OH) + PBr_3 = 3\,C_2H_5Br + PH_3O_3.$$

They are also formed by the action of chlorine and bromine on the saturated hydrocarbons, and by the addition of the halogen-hydric acids to the unsaturated hydrocarbons. In the latter case the halogen unites with the carbon atom which holds the least hydrogen :

$$CH_3{-}CH{=}CH_3 + HI = CH_3{-}CHI{-}CH_3$$
$$CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{=}CH_2 + HI = CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}I{-}CH_3$$

The dichlorides, dibromides, and di-iodides are produced by leading chlorine, bromine, or iodine, into either the hydrocarbons of the series C_nH_{2n}, in which case the two halogens take up with two different carbon atoms; or into the monochlorides, bromides, or iodides, in which case both the halogens unite with the same carbon atom :

$$CH_2{=}CH_2 + Cl_2 = CH_2Cl{-}CH_2Cl$$
$$CH_3CH_2Cl + Cl_2 = CH_3{-}CHCl_2 + HCl.$$

The other chlorides, etc., are formed by the continued action of chlorine, etc., on the alkylogens.

On treatment with moist silver oxide, the halogens are replaced by hydroxyl, forming alcohols, glycols, aldehydes, etc.:

$$2\,CH_3{-}CH_2Cl + Ag_2O + H_2O = 2\,CH_3{-}CH_2(OH) + 2\,AgCl$$
$$CH_2Cl{-}CH_2Cl + Ag_2O + H_2O = CH_2(OH){-}CH_2(OH) + 2\,AgCl$$
$$CH_3{-}CHCl_2 + Ag_2O = CH_3{-}CHO + 2\,AgCl.$$

On digestion with a silver salt, an ester (compound ether) is obtained :

$$C_2H_5Cl + C_2H_3O_2Ag = \underset{\text{Acetic ester}}{C_2H_5{-}C_2H_3O_2} + AgCl.$$
$$C_2H_4Cl_2 + 2\,C_2H_3O_2Ag = C_2H_4{=}(C_2H_3C_2)_2 + AgCl.$$

On digestion with potassium salts, the halogen is replaced by the rest in combination with potassium :

$$C_2H_5Cl + KCN = C_2H_5{-}CN$$
$$C_2H_5Cl + KSCN = C_2H_5{-}SCN, \text{ etc.}$$

Nascent hydrogen converts the halogen derivatives back into the hydrocarbons.*

Hydroxyl Derivatives.

1) Alcohols.

a) Monohydric alcohols, $C_nH_{2n+1}OH$:

$CH_4O = CH_3OH$ Methyl alcohol, B. p. 65°

$C_2H_6O = CH_3{-}CH_2OH$ Ethyl alcohol, B. p. 79°

$C_3H_8O =$
- $CH_3{-}CH_2{-}CH_2OH$ Propyl alcohol, B. p. 97°
- $CH_3{-}CH(OH){-}CH_3$ Isopropyl alcohol, B. p. 83°

$C_4H_{10}O$
- $CH_3{-}CH_2{-}CH_2{-}CH_2(OH)$ Butyl alcohol, B. p. 117°
- $CH_3{-}CH_2{-}CH(OH){-}CH_3$ Secondary butyl alcohol, B. p. 980°
- $CH_3{-}CH(CH_3){-}CH_2(OH)$ Isobutyl-alcohol, B. p. 108°
- $CH_3{-}C(CH_3)(OH){-}CH_3$ Trimethyl-carbinol, B. p. 82°

$C_5H_{12}O$
- $CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2(OH)$ Normal amyl alcohol, B. p. 137°
- $CH_3{-}CH_2{-}CH_2{-}CH(OH){-}CH_3$ Propyl-methyl-carbinol, B. p. 119°
- $(C_2H_5){-}CH(OH){-}C_2H_5$ Di-ethyl-carbinol, B. p. 117°
- $CH_3{-}CH(CH_3){-}CH_2{-}CH_2(OH)$ Ordinary amyl alcohol, B. p. 130°
- $CH_3{-}CH(OH){-}CH(CH_3){-}CH_3$ Isopropyl-methyl-carbinol, B. p. 108°
- $CH_3{-}CH_2{-}C(OH)(CH_3){-}CH_3$ Ethyl-dimethyl-carbinol, B. p. 97°

*The action of iodohydric acid is both substituting and reducing. Glycerol and HI yield isopropyl iodide:

$C_6H_{14}O$	$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}OH$	Normal hexyl alcohol, B. p. 158°
	$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH(OH){-}CH_3$	Butyl-methyl-carbinol, B. p. 137°
	$CH_3{-}CH_2{-}CH_2{-}CH(OH){-}CH_2{-}CH_3$	Propyl-ethyl-carbinol, B. p. 134°
	$(CH_3)_3{\equiv}C{-}CH(OH){-}CH_3$	Pinacolyl alcohol, B. p. 120.5°
	$(CH_3)_2{=}C(OH){-}C_3H_7$	Propyl-dimethyl-carbinol, B. p. 115°
	$(CH_3)_2{=}C(OH){-}CH(CH_3)_2$	Isopropyl-dimethyl-carbinol, B. p. 113°
	$(C_2H_5)_2{=}C(OH){-}CH_3$	Di-ethyl-methyl-carbinol, B. p. 120°
$C_7H_{16}O$	$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2(OH)$	Normal heptyl alcohol, B. p. 175°
	$(C_3H_7)_2{=}CH(OH)$	Dipropyl-carbinol, B. p. 150°
	$(CH_3)_2{=}CH{-}CH(OH){-}CH(CH_3)_2$	Di-isopropyl-carbinol, B. p. 132°
	$(C_2H_5)_3{\equiv}C(OH)$	Tri-ethyl-carbinol, B. p. 142°
	$(CH_3)_2{=}C(OH){-}CH_2{-}CH(CH_3)_2$	Dimethyl-isobutyl-carbinol, B. p. 130°
	$(CH_3)_3{\equiv}C{-}C(OH){=}(CH_3)_2$	Penta methyl-ethol, B. p. 132°
$C_8H_{18}O$	Normal octyl alcohol,	B. p. 192°
	Hexyl-methyl-carbinol,	B. p. 179°
	Propyl-di-ethyl-carbinol,	B. p. about 150°
$C_9H_{20}O$	Nonyl alcohol,	B. p. about 200°
$C_{10}H_{22}O$	Decatyl alcohol,	B. p. about 212°

$CH_2(OH){-}CH(OH){-}CH_2(OH) + 5\ HI = CH_3{-}CHI{-}CH_3 + 3\ H_2O + 2\ I_2.$

Erythrol yields secondary butyl iodides. Chloroform gives methylene iodide:

$$CHCl_3 + 4\ HI = CH_2I_2 + 3\ HCl + I_2.$$

$C_{16}H_{33}(OH)$ Cetyl alcohol
$C_{27}H_{55}(OH)$ Cerotyl alcohol
$C_{30}H_{61}(OH)$ Myricyl alcohol
} solid at ordinary temperatures.

The constitution of the last six alcohols is not known. The number of possible isomers is very great.

Finally, $C_nH_{2n-1}OH$:

$$C_3H_6O = \underset{\text{Allyl alcohol}}{CH_2{=}CH{-}CH_2OH}.$$

Ethers of these alcohols, $C_nH_{2n+2}O$:

$C_2H_6O = CH_3{-}O{-}CH_3$ Methyl-ether, B. p. $-21°$
$C_3H_8O = CH_3{-}O{-}C_2H_5$ Methyl-ethyl-ether, $+11°$
$C_4H_{10}O = C_2H_5{-}O{-}C_2H_5$ Ethyl-ether, $+35.5°$
$C_6H_{14}O = C_4H_9{-}O{-}C_2H_5$ Butyl-ethyl-ether, etc.

b) Dihydric alcohols, glycols, $C_nH_{2n}(OH)_2$:

$C_2H_6O_2 = CH_2(OH){-}CH_2(OH)$ Ethyl-glycol
$C_3H_8O_2 = \begin{cases} CH_2(OH){-}CH_2{-}CH_2(OH) & \text{Propyl-glycol} \\ CH_3{-}CH(OH){-}CH_2(OH) & \text{Isopropyl-glycol} \end{cases}$
$C_4H_{10}O_2$ Butyl-glycol
$C_5H_{12}O_2$ Amyl-glycol.

c) Trihydric alcohols, glycerols, $C_nH_{2n-1}(OH)_3$:

$C_3H_8O_3 = CH_2(OH){-}CH(OH){-}CH_2(OH)$ Glycerol
$C_5H_{12}O_3$ Isoamylglycerol.

d) Tetrahydric alcohols, $C_nH_{2n-2}(OH)_4$:

$C_4H_{10}O_4 = CH_2(OH){-}CH(OH){-}CH(OH){-}CH_2(OH)$
Erythrol.

e) Hexahydric alcohols :

$C_6H_{14}O_6$. Mannol, Dulcol.

The alcohols can be produced from their corresponding aldehydes, or acid anhydrides, by the action of nascent hydro-

gen, or from the chlorides, bromides, etc., of the hydrocarbons by the action of moist silver oxide. They can also be obtained by treating the alkylogens with the salt of an organic acid, and decomposing the resulting ester with potassium hydroxide:

$$\underset{\text{Allyl iodide}}{C_3H_5I} + \underset{\text{Sodium acetate}}{C_2H_3NaO_2} = \underset{\text{Acetic allyl ester}}{C_2H_3(C_3H_5)O_2} + NaI.$$

$$C_2H_3(C_3H_5)O_2 + KHO = \underset{\text{Potassium acetate}}{C_2H_3KO_2} + \underset{\text{Allyl alcohol}}{C_3H_5(OH)}.$$

Besides the above methods, they are formed by the action of the zinc compounds of the hydrocarbons on the aci-chlorides (p. 93):

$$CH_3{-}COCl + 2\,Zn(CH_3)_2 + 3\,H_2O = (CH_3)_3{\equiv}C{-}OH + ZnClOH + Zn(OH)_2 + 2\,CH_4,$$

and by the action of zinc on a mixture of the iodide and the formic ester:

$$CHO{-}OC_2H_5 + 4\,CH_3I + 3\,Zn + 3\,H_2O = (CH_3)_2{=}CH(OH) + 2\,ZnI + Zn(OH)_2 + 2\,CH_4 + C_2H_6O.$$

Alcohols are divided into three classes, viz.: *primary alcohols*, which on oxidation yield the aldehyde and the acid of the same carbon series; *secondary alcohols*, which on oxidation yield a ketone of the same carbon series, and by further oxidation yield acids of lower carbon series; and *tertiary alcohols*, which break at once by oxidation into acids of lower series. The secondary and tertiary alcohols easily lose the elements of water, affording hydrocarbons of the C_nH_{2n} series. Among the isomeric alcohols, the normal possess the highest boiling point, the primary higher than the secondary, and the latter higher than the tertiary. Regularities seem to exist in the differences between the boiling points of homologous alcohols, but a law is not yet known.

The ethers are made from the alcohols by the action of their chlorides, etc., on the sodium compound of the alcohol, or by treatment of the alcohols with sulphuric acid (see p. 26).

2. a) Aldehydes, $C_nH_{2n+1}CHO$:

CH_2O =	$H\text{-}CHO$	Methaldehyde	
C_2H_4O =	$CH_3\text{-}CHO$	Ethaldehyde	21° b. p.
C_3H_6O =	$CH_3\text{-}CH_2\text{-}CHO$	Propionaldehyde	59.5°
C_4H_8O =	$CH_3\text{-}CH_2\text{-}CH_2\text{-}CHO$	Butyraldehyde	75°
	$CH_3\text{-}CH(CH_3)\text{-}CHO$	Isobutyraldehyde	68°
$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CHO$		Normal valeraldehyde	102°
$CH_3\text{-}CH(CH_3)\text{-}CH_2\text{-}CHO$		Fermentation valeraldehyde	93°
$C_6H_{12}O$		Caproic aldehyde	121°
$C_7H_{14}O$		Œnanthaldehyde.	

The aldehydes are formed by the oxidation of the primary alcohols, or by the distillation of the lime salts of the corresponding acid with calcium formate. Nascent hydrogen converts them into primary alcohols. They are easily oxidized into their corresponding acids, not only by the ordinary oxidizing agents, but also by silver oxide. A part of the silver goes into combination with the acid, while the remainder is precipitated as a mirror on the inner surface of the vessel.

The aldehydes polymerize very easily, two or three molecules uniting to a single one. It is supposed that this polymerization takes place in the following manner. One of the bindings between the carbon and the oxygen breaks. Both the carbon and oxygen thus have a free valence. These free bonds are then neutralized by the free bonds of another similar molecule, the bond of the carbon being satisfied by the bond of the oxygen and the bond of the oxygen by that of the carbon:

$CH_3\text{-}CHO$ gives $H_3C\text{-}CH(O\text{-}CH(O\text{-}CH)\text{-}CH_3)\text{-}O$

Ethyl aldehyde — Paraldehyde

In a similar manner, two molecules of aldehyde condense with elimination of water to one molecule:

$2\,CH_3\text{-}CHO$ give $CH_3\text{-}CH{=}CH\text{-}CHO$ and H_2O.

Crotonaldehyde

b) Ketones, $C_nH_{2n+2}CO$:

C_3H_6O =	$CH_3{-}CO{-}CH_3$	Acetone	58°
C_4H_8O =	$CH_3{-}CO{-}C_2H_5$	Methylethylketone	81°
$C_5H_{10}O$ =	$CH_3{-}CO{-}C_3H_7$	Methylpropylketone	103°
	$C_2H_5{-}CO{-}C_2H_5$	Diethylketone	104°
	$CH_3{-}CO{-}CH(CH_3)_2$	Methylisopropylketone	93.5°, etc.

Ketones are formed by the oxidation of secondary alcohols, and by the distillation of salts of organic acids. Nascent hydrogen converts them into secondary alcohols. On oxidation, they fall into two acids of lower carbon content, the CO-group remaining with the smaller rest :

$$CH_3{-}CO{-}CH_3 + 3\,O = CHOOH + CH_3{-}COOH$$
$$C_3H_7{-}CO{-}CH_3 + 3\,O = C_3H_6O_2 + CH_3{-}COOH.$$

The ketones also have the property of condensing with elimination of water :

$$2\,CH_3{-}CO{-}CH_3 = CH_3{-}C{-}CH_3$$
$$\overset{\|}{C}H{-}CO{-}CH_3 + H_2O.$$

Mesityl-oxide

3. a) Monobasic acids, $C_nH_{2n+1}COOH$:

CH_2O_2 =	HCOOH	F. p. + 8°	Formic acid	B. p. 99°
$C_2H_4O_2$ =	$CH_3{-}COOH$	" + 17°	Acetic acid	" 118°
$C_3H_6O_2$ =	$CH_3{-}CH_2{-}COOH$		Propionic acid	" 141°
$C_4H_8O_2$ =	$CH_3{-}CH_2{-}CH_2{-}COOH$		Butyric acid	" 163°
	$CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}H{-}COOH$		Isobutyric acid	" 154°
$C_5H_{10}O_2$ =	$CH_3{-}CH_2{-}CH_2{-}CH_2{-}COOH$		Normal valerianic acid	" 185°
	$CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}H{-}CH_2{-}COOH$		Valerianic acid	" 175°
$C_6H_{12}O_2$ =	Normal caproic acid,			" 205°
	Isocaproic acid,			" 200°

$C_7H_{14}O_2$	Œnanthylic acid,	B. p. 224°	
$C_8H_{16}O_2$	Caprylic acid,	B. p. 236°	F. p. 17°
$C_9H_{18}O_2$	Pelargonic acid,	B. p. 254°	F. p. 12°
$C_{10}H_{20}O_2$	Capric acid,	B. p. 270°	F. p. 30°
$C_{12}H_{24}O_2$	Lauric acid,		F. p. 44°
$C_{14}H_{28}O_2$	Myristic acid,		F. p. 54°
$C_{16}H_{32}O_2$	Palmitic acid,		F. p. 62°
$C_{17}H_{34}O_2$	Margaric acid,		F. p. 60°
$C_{18}H_{36}O_2$	Stearic acid,		F. p. 69°
$C_{20}H_{40}O_2$	Arachidic acid,		F. p. 75°
$C_{22}H_{44}O_2$	Behenic acid,		F. p. 76°
$C_{25}H_{50}O_2$	Hyaenic acid,		F. p. 77°
$C_{27}H_{54}O_2$	Cerotic acid,		F. p. 79°
$C_{30}H_{60}O_2$	Melissic acid,		F. p. 91°

The lower members of these acids, up to capric acid, are, with the exception of acetic acid, liquid at ordinary temperatures. They can be distilled without decomposition, and produce on paper a grease-spot which vanishes on standing. They are soluble in water, but their solubility decreases with their increasing content of carbon, so that the latter members are very difficultly soluble.

The higher members are solid, insoluble in water and soluble in alcohol and ether. They produce a grease-spot on paper, which does not disappear. They cannot be distilled without decomposition.

These acids are formed by the oxidation of their corresponding primary alcohols and aldehydes, and by boiling the proper cyanides with bases or acids:

$$\underset{\text{Ethyl cyanide}}{C_2H_5CN} + KOH + H_2O = \underset{\text{Potassium propionate}}{C_2H_5CO_2K} + NH_3.$$

They are also produced by boiling their esters with bases:

$$\underset{\text{Stearin}}{C_3H_5(OC_{18}H_{35}O)_3} + 3\,KOH = \underset{\text{Glycerol}}{C_3H_5(OH)_3} + 3\,\underset{\text{Potassium stearate}}{C_{18}H_{35}KO_2}.$$

Lastly, they are obtained by the action of the chlorides, etc., on sodium aceto-acetic ester, and decomposition of the substituted aceto-acetic ester thus obtained with potassium hydroxide. (Compare p. 92.)

The acids are converted by the action of phosphorus pentachloride into *aci-chlorides,* the OH being replaced by Cl :

$$CH_3{}^-COOH + PCl_5 = POCl_3 + CH_3COCl + HCl.$$

The aci-chlorides can also be produced by the action of phosphorus oxychloride on a salt of the acid. Their Cl is very easily replaced by other elements or groups. With water, the acid is regenerated.

The *anhydrides* of the acids are obtained by the action of the aci-chloride on a salt of the acid :

$$CH_3{}^-COCl + CH_3{}^-COONa = NaCl + CH_3{}^-CO{}^-O{}^-CO{}^-CH_3,$$

or by the action of phosphorus oxychloride on an excess of a salt of the acid :

$$4\,CH_3{}^-COONa + POCl_3 = NaPO_3 + 3\,NaCl + 2\,(CH_3CO)_2O.$$

Acetic anhydride

The acid anhydrides are easily decomposed. With water, they yield the original acid.

Phosphorus pentasulphide converts the acids into *thio-acids :*

$$5\,CH_3{}^-COOH + P_2S_5 = P_2O_5 + 5\,CH_3{}^-COSH.$$

Thioacetic acid

Thio-acids are decomposed by water into H_2S and the original acid. With alcohol, they produce the mercaptan and the acid :

$$CH_3{}^-COSH + H_2O = H_2S + CH_3{}^-COOH$$
$$CH_3{}^-COSH + C_2H_5HO = C_2H_5SH + CH_3{}^-COOH.$$

The specific gravity of the lower fatty acids decreases with the content of carbon :

Acetic acid,	Sp. gr. 1.05	Caproic acid,	Sp. gr. 0.93
Propionic acid,	" 0.99	Heptylic acid,	" 0.92
Butyric acid,	" 0.95	Octylic acid,	" 0.91
Valerianic acid,	" 0.94	Nonylic acid,	" 0.90

$C_nH_{2n-1}COOH$:

$C_3H_4O_2 = CH_2{=}CH{-}COOH$ Acrylic acid B. p. 140°

$C_4H_6O_2 =$
- $CH_3{-}CH{=}CH{-}COOH$ Crotonic acid " 182°
- $CH_2{=}CH{-}CH_2{-}CO_2H$ Isocrotonic acid " 172°
- $CH_2{=}C<^{CO_2H}_{CH_3}$ Methylacrylic acid " 160°

$C_5H_8O_2$
- Angelic acid F. p. 45° B. p. 185°
- Tiglic acid " 65° " 198.5°

$C_6H_{10}O_2$
- Hydrosorbic acid " 208.5°
- Pyroterebic acid " 207°
- Ethylcrotonic acid F. p. 41°

$C_{16}H_{30}O_2$ Hypogæic acid " 33°

$C_{18}H_{34}O_2$ Oleïc acid " 14°

$C_{22}H_{42}O_2$ Erucic acid " 34°

These acids are distinguished from the preceding ones containing the same amount of carbon, by containing two atoms of hydrogen less. They are hence unsaturated acids, and have the power of uniting with two atoms of Cl, Br, or I. They break on fusion with KOH into two acids of lower series, the molecule generally breaking at the double binding:

$$CH_2{=}CH{-}COOH + 2\,KHO = \underset{\text{Potassium formate}}{CHKO_2} + \underset{\text{Potassium acetate}}{C_2H_3KO_2} + 2\,H.$$

The higher acids of this series are called *oil-acids*.

b) Monobasic acids containing alcoholic hydroxyl, glycollic acids, $C_nH_{2n}(OH)COOH$:

$C_2H_4O_3 = CH_2(OH){-}COOH$ Glycollic acid

$C_3H_6O_3 =$
- $CH_2(OH){-}CH_2{-}COOH$ Paralactic acid
- $CH_3{-}CH(OH){-}COOH$ Lactic acid

$C_4H_8O_3$ Butylactic acid

$C_6H_{12}O_3$ Leucic acid

c) Dibasic acids, $C_nH_{2n+2}(COOH)_2$:

$C_2H_2O_4$	Oxalic acid	
$C_3H_4O_4$	Malonic acid	F. p. 132°
C_4H_6O	Succinic acid	" 180°
	Isosuccinic acid	" 130°
$C_5H_8O_4$	Glutaric acid	" 97°
	Pyrotartaric acid	" 112°
	Ethyl-malonic acid	" 112°
	Dimethyl-malonic acid	" 170°
$C_6H_{10}O_4$	Adipic acid	" 148°
$C_7H_{12}O_4$	Pimelic acid	" 114°
$C_8H_{14}O_4$	Suberic acid	" 140°
$C_{10}H_{18}O_4$	Sebacic acid	" 127°
$C_{17}H_{32}O_4$	Rocellic acid	" 132°

d) Dibasic acids with alcoholic hydroxyl :

$$C_4H_6O_5 = \begin{matrix} CH_2\text{-}COOH \\ | \\ CH(OH)\text{-}COOH \end{matrix}$$ Malic acid

$$C_4H_6O_6 = \begin{matrix} CH(OH)\text{-}COOH \\ | \\ CH(OH)\text{-}COOH \end{matrix}$$ Tartaric acid.

e) Tribasic acids :

$C_6H_8O_7$, Citric acid.

When the salt of an organic acid, either alone or mixed with the salt of another organic acid, is submitted to dry distillation, a ketone is produced. If one of the salts is a formate, an aldehyde is obtained. An aldehyde may be considered as a ketone in which one of the hydrocarbon rests is replaced by H (compare p. 112).

4) Esters (compound ethers) :

$C_2H_4O = CHO_2\text{-}CH_3$ Methyl formic ester B. p. 33°

$C_3H_6O_2 = \begin{cases} CHO_2{-}C_2H_5 & \text{Ethyl formic ester} \quad \text{B. p. } 55° \\ C_2H_3O_2{-}CH_3 & \text{Methyl acetic ester} \quad 55° \end{cases}$

$C_4H_8O_2 = \begin{cases} CHO_2{-}C_3H_7 & \text{Propyl formic ester} \quad 77° \\ C_2H_3O_2{-}C_2H_5 & \text{Ethyl acetic ester} \\ C_3H_5O_2{-}CH_3 & \text{Methyl propionic ester} \end{cases}$

$C_5H_{10}O_2 = \begin{cases} CHO_2{-}C_4H_9 & \text{Isobutyl formic ester} \quad \text{abt. } 100° \\ C_2H_3O_2{-}C_3H_7 & \text{Propyl acetic ester} \quad 102° \\ C_3H_5O_2{-}C_2H_5 & \text{Ethyl propionic ester} \quad 99° \\ C_4H_7O_2{-}CH_3 & \text{Methyl butyric ester} \quad 95°, \text{ etc.} \end{cases}$

The higher members of the esters form many isomers. They are isomeric with the fatty acids, from which their constitution differs chiefly in their possessing a carbon atom which is not bound directly to another carbon atom, but is linked by means of an atom of oxygen. They are made (1) by distilling a salt of a fatty acid (usually a sodium or silver salt) with a mixture of sulphuric acid and the alcohol; (2) By digesting the salt with the chloride, bromide, or iodide of a hydrocarbon; (3) By saturating a mixture of the acid and alcohol with chlorhydric acid gas and distilling. On boiling with a solution of potassium or sodium hydroxide, they are decomposed into the salt of the acid and the alcohol. Ammonia converts them into the amide and alcohol.

Amine Bases.

$CH_3{-}NH_2$	Methylamine	
$(CH_3)_2NH$	Dimethylamine	
$(CH_3)_3N$	Trimethylamine	B. p. 9°
$C_2H_5{-}NH_2$	Ethylamine	B. p. 19°
$(C_2H_5)(CH_3)NH$	Methylethylamine	
$(C_2H_5)_2NH$	Diethylamine	B. p. 57°
$(C_2H_5)_3N$	Triethylamine	B. p. 96°
$C_3H_7(NH_2)$	Propylamine and Isopropylamine	

$C_4H_9(NH_2)$	Butylamine and Isobutylamine
$C_5H_{11}(NH_2)$	Amylamine
$(C_5H_{11})_2NH$	Diamylamine
$(C_5H_{11})_3N$	Triamylamine
$\begin{matrix}CH_2(NH_2)\\ \vert\\ CH_2(NH_2)\end{matrix}$	Ethylenediamine
$\begin{matrix}CH_2\text{-}NH\text{-}CH_2\\ \vert\quad\quad\vert\\ CH_2\text{-}NH\text{-}CH_2\end{matrix}$	Diethlenediamine, etc.

The amines possess basic properties, form salts with acids, and give with platinic chloride difficultly soluble double salts, *e.g.* $(CH_3\text{-}NH_2.HCl)_2PtCl_4$.

The ammonium bases, $(CH_3)_4NI$, are characteristic of the penta-valence of nitrogen.

The primary amine bases can be converted into the secondary, the latter into the tertiary, and these into the ammonium compounds. The amines can be distilled without decomposition, but the ammonium bases break thereby into tertiary amines, hydrocarbons of the series C_nH_{2n} and water:

$$\underset{\text{Tetra-ethyl ammonium hydroxide}}{(C_2H_5)_4NOH} = \underset{\text{Tri-ethylamine}}{(C_2H_5)_3N} + \underset{\text{Ethylene}}{C_2H_4} + H_2O.$$

The only exception to this rule is tetramethylammonium hydroxide, which yields CH_4O, methyl alcohol, instead of CH_2, H_2O and trimethylamine.

We can ascertain whether an amine is primary, secondary or tertiary, by attempting to convert it into the tetra-substituted ammonium salt. The base, C_3H_9N, for instance, may be trimethylamine, $(CH_3)_3N$, (tertiary); or methylethylamine, $CH_3\text{-}NH\text{-}C_2H_5$, (secondary); or propylamine, $C_3H_7\text{-}NH_2$, (primary). On digestion with ethyl iodide to saturation, we obtain in the first case a compound $(CH_3)_3(C_2H_5)NI$; in the second case, $C_2H_5(CH_3)(C_2H_5)_2NI$; in the third case, $C_3H_7(C_2H_5)_3NI$. These are all different bodies. If, therefore, only one H can be substituted by an ethyl-group,

the compound is a tertiary amine, if two H's, a secondary, if three, a primary.

In the same manner that amines are derived from alcohols by the replacement of the hydroxyl by the amido-group, amides are derived from acids by the replacement of the hydroxyl of the carboxyl by the amido-group :

$CH_3{-}CH_2(OH)$ Ethyl alcohol	$CH_3{-}CH_2(NH_2)$ Ethylamine
$CH_3{-}CO(OH)$ Acetic acid	$CH_3{-}CO(NH_2)$ Acetamide

$CHO{-}NH_2$	Formamide
$CH_3{-}CO{-}NH_2$	Acetamide
$(CH_3{-}CO)_2NH$	Diacetamide
$(CH_3{-}CO)_3N$	Triacetamide.

The phosphines, stibines, and arsines correspond in constitution to the amines.

Cyanides.

$CH_3{-}CN$	Methyl cyanide,	Acetonitrile
$C_2H_5{-}CN$	Ethyl cyanide,	Propionitrile
$C_3H_7{-}CN$	Propyl cyanide,	Butyronitrile
$C_4H_9{-}CN$	Butyl cyanide,	Valeronitrile.

The cyanides are obtained by the action of potassium cyanide on the chlorides, etc., of the hydrocarbons. On boiling with acids or alkalis, they are converted into the acids of the next higher series (and ammonia) :

$CH_3{-}NC$	Methyl isocyanide
$C_2H_5{-}NC$	Ethyl isocyanide
$C_3H_7{-}NC$	Propyl isocyanide
$C_4H_9{-}NC$	Butyl isocyanide, etc.

The isocyanides are formed together with the cyanides. They are also produced by the action of two molecules of silver cyanide, one molecule of an iodide, or by the action of

chloroform on the primary amines in the presence of potassium hydroxide. They decompose easily into the amines and formic acid.

Corresponding to two series of cyanides, there are two series of cyanates and sulphocyanates :

$CH_3{-}N{=}CO$	Methyl cyanate
$CH_3{-}O{-}CN$	Methyl isocyanate
$CH_3{-}N{=}CS$	Methyl mustard oil
$CH_3{-}S{-}CN$	Methyl sulphocyanate, etc.

Nitro-Compounds.

These compounds, which are isomeric with the nitrous esters, are obtained by the action of silver nitrite on the iodides. Nascent hydrogen converts them into amines.

Sulphonic Acids.

$CH_3{-}SO_3H$	Methyl sulphonic acid
$C_2H_5{-}SO_3H$	Ethyl sulphonic acid
$C_3H_7{-}SO_3H$	Propyl sulphonic acid
$CH_2{=}(SO_3H)_2$	Methylene sulphonic acid.

The sulphonic acids are isomeric with the primary sulphurous esters. Their ammonium salts are obtained by digesting neutral ammonium sulphite with the alkylogens.

There remain still to be mentioned, the metallo-compounds of the hydrocarbons, of which the zinc and mercury compounds are the principal.

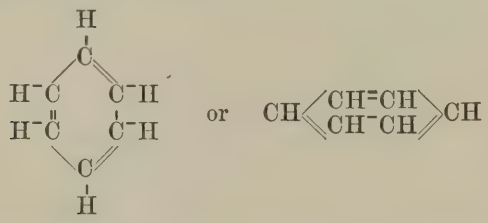
$(CH_3)_2Zn$	Zinc methyl
$(C_2H_5)_2Zn$	Zinc ethyl
$(CH_3)_2Hg$	Mercury methyl
$(C_2H_5)_2Hg$	Mercury ethyl.

They are produced by the action of the metal on the iodides. Owing to the great ease with which the metal is substituted by other elements or atomic groups, they are well suited to the production of new compounds.

Aromatic Compounds.

We come now to a class of compounds which differ considerably in their behavior from the substances we have thus far considered, and which are generally termed the fatty series. On the average, the aromatic compounds are richer in carbon than the fatty compounds. The chief products which they yield on decomposition belong to the same class. They cannot be converted into the fatty compounds without suffering the most vital decomposition of the molecule. Neither can the fatty compounds be converted into the aromatic compounds except by reactions which cannot be represented by chemical formulas.

While the fatty compounds are derived from methane, the aromatic compounds are derived from a hydrocarbon of the formula, C_6H_6, which belongs to the C_nH_{2n-6} series. The most generally adopted constitution of this body is that each of the six carbon atoms is bound to two other carbon atoms, to one of them by one bond, to the other by two bonds, forming a closed chain, or ring.

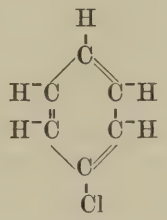


This hydrocarbon is called *benzene*. A hydrogen atom is united to each carbon atom. The ring cannot be broken by

ordinary reactions. The double binding, however, can be dissolved and another mono-valent atom united with each carbon atom.

The six hydrogen atoms on the benzene ring are capable of substitution, and far more easily than those of methane.

If we replace a hydrogen atom by chlorine, we shall obtain C_6H_5Cl:



No matter with which carbon atom the chlorine unites, it is surrounded by five hydrogen atoms. In every case it has the same position. Hence, only one compound of the formula, C_6H_5Cl, is possible. The same is the case when instead of the chlorine we have a hydroxyl-group, C_6H_5OH; or an amido-group, $C_6H_5NH_2$; or a methyl-group, $C_6H_5CH_3$; or a carboxyl-group, C_6H_5 COOH. If only one atom of hydrogen of the benzene nucleus is replaced by a mono-valent element, or atomic group, no matter how complicated it may be, only one compound is possible.

We shall mention here a chemically characteristic peculiarity of the aromatic hydrocarbons and their derivatives, which sharply defines them from the fatty compounds. We have seen that the hydrogen of the fatty compounds is substituted *directly* only with difficulty. Chlorine and bromine, it is true, have the power of substituting the hydrogen, but to produce new derivatives, it is necessary to use the chlorides, bromides or iodides, or salts of the primary sulphuric esters. It is particularly to be remarked that when nitric, or sulphuric

acids act on the fatty compounds, the hydrogen of the fatty compound does not unite with the hydroxyl of the acid to form water and a substitution product arising from the replacement of the H of the fatty compound by the rest of the acid (*i. e.*, the acid minus hydroxyl). Nitric acid, for instance, does not yield with methane, water and a compound $CH_3{-}NO_2$, nitromethane,

$$CH_4 + NO_2OH \quad \text{does not yield} \quad CH_3NO_2 + H_2O.$$

Neither does sulphuric acid produce a sulphonic acid :

$$CH_4 + SO_2\langle{}^{OH}_{OH} \quad \text{does not yield} \quad SO_2\langle{}^{CH_3}_{OH} + H_2O.$$

Nitromethane and methylsulphonic acid are both known, but they are formed by entirely different reactions, the former by the action of silver nitrite on methyl iodide, and the latter by the action of ammonium sulphite on methyl iodide (compare p. 39).

The aromatic bodies, however, behave in a very different manner. Their hydrogen is easily replaced by the rests of nitric and sulphuric acids, so that the nitro- and sulphonic acid derivatives can be obtained by direct action. The only fatty compounds acted on by nitric and sulphuric acids are the alcohols, and the products are esters. The difference between the nitro- and sulphonic acid compounds and the esters lies in the carbon and sulphur being bound directly with the carbon in the former, while in the latter they are not bound directly, but linked by means of oxygen :

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + \underset{\text{Sulphuric acid}}{SO_2\langle{}^{OH}_{OH}} = \underset{\text{Ethyl sulphuric acid}}{SO_2\langle{}^{OC_2H_5}_{OH}} + H_2O$$

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Sulphuric acid}}{SO_2\langle{}^{OH}_{OH}} = \underset{\text{Benzene sulphonic acid}}{SO_2\langle{}^{C_6H_5}_{OH}} + H_2O$$

$$2\,C_2H_5OH + SO_2\langle{}^{OH}_{OH} = \underset{\text{Ethyl sulphuric ester}}{SO_2\langle{}^{OC_2H_5}_{OC_2H_5}} + 2\,H_2O$$

$$2\,C_6H_6 + SO_2\langle{}^{OH}_{OH} = SO_2\langle{}^{C_6H_5}_{C_6H_5} + 2\,H_2O$$

Sulphobenzide

$$C_2H_5OH + NO_2OH = NO_2{}^-O{}^-C_2H_5 + H_2O$$

Ethyl nitric ester

$$C_6H_6 + NO_2OH = NO_2{}^-C_6H_5 + H_2O.$$

Nitrobenzene

The difference between the nitro- and sulphonic acid compounds, and the nitrous and sulphurous esters isomeric with them, appears plainly in the products which are formed by their reduction with nascent hydrogen.

N^-CH_3 isomeric with $O{=}N^-O^-CH_3$. Both are CH_3NO_2.

Nitromethane — Methyl nitrous ester

$HO^-S^-CH_3$ isomeric with $CH_3{}^-O^-S^-H$. Both are CH_4SO_3.

Methylsulphonic acid — Methyl sulphurous ester

When the nitrogen and sulphur are bound directly to carbon, as is the case with the nitro- and sulphonic acid compounds, these elements remain bound to the carbon on reduction, and the oxygen which was in combination with them is replaced by hydrogen :

$$N^-CH_3 \text{ gives } H_2N^-CH_3 + 2\,H_2O,$$

Methylamine

$$HO^-S^-CH_3 \text{ gives } HS^-CH_3 + 3\,H_2O\,;$$

Methyl mercaptan.

When, however, the binding is not direct but indirect, *i.e.*, consists of a linking by oxygen, as is the case in the nitrous and sulphurous esters, the nitrogen and sulphur break off, the hydrogen unites with the oxygen, and an alcohol is produced :

$$O{=}N^-O^-CH_3 \text{ gives } HOCH_3 + NH_3 + H_2O,$$

Methyl alcohol

$$CH_3{}^-O^-S^-H \text{ gives } HOCH_3 + H_2S + 2\,H_2O.$$

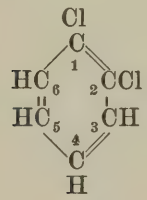
Methyl alcohol

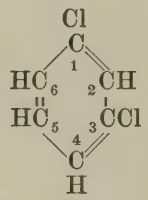
Many benzene derivatives yield with nitrous acid, or its esters, compounds in which an H of the benzene-nucleus is replaced by the rest of

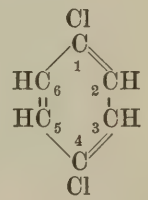
nitrous acid, NO. These derivatives are called *nitroso-compounds.* Nitric acid oxidizes them to nitro-compounds.

We have seen that there can be only one chlorbenzene, one hydroxylbenzene, one nitrobenzene, one benzene sulphonic acid, one methylbenzene, one carboxylbenzene, &c.

The case is different, however, when two hydrogen atoms of benzene are replaced by two mono-valent atoms, or groups, as the relative position of the two substituting elements has a great influence on the nature of the compound which is formed. Let us take the simplest case, the one in which two atoms of the hydrogen in benzene are replaced by two chlorine atoms. We find that there are three modifications of this compound :

1) 

2) 

3) 

Or 1) CCl . CCl . CH . CH . CH . CH
2) CCl . CH . CCl . CH . CH . CH
3) CCl . CH . CH . CCl . CH . CH

If we represent the upper C by 1, and count to the right, we can represent these compounds as follows :

1) $C_6H_4 \left\{ \begin{matrix} 1\,Cl \\ 2\,Cl' \end{matrix} \right.$ 2) $C_6H_4 \left\{ \begin{matrix} 1\,Cl \\ 3\,Cl' \end{matrix} \right.$ 3) $C_6H_4 \left\{ \begin{matrix} 1\,Cl \\ 4\,Cl' \end{matrix} \right.$

A fourth compound is not possible, since 1 . 5 is the same as 1 . 3, both of the chlorine atoms being separated by an H. In the same manner 1 . 6 is the same as 1 . 2. The two entering atoms, or groups, are, then, either adjacent (1 . 2, 1 . 6), or separated by one H (1 . 3, 1 . 5), or separated by two H's (1 . 4). In the latter case they are directly opposite.

Consequently there are theoretically possible :

Three dichlorbenzenes,
Three dihydroxylbenzenes,
Three diamidobenzenes,
Three chlorhydroxylbenzenes,
Three chloramidobenzenes,
Three amidonitrobenzenes,
Three dinitrobenzenes, etc.

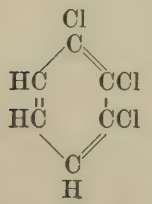
The di-substitutions of benzene are classified as follows: When the substitutions are adjacent (1 . 2, 1 . 6), the compound is called *ortho ;* when separated by one H (1 . 3, 1 . 5), *meta ;* when separated by two H's (1 . 4) *para.* In writing the formulas, the names are expressed by small letters :

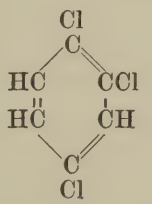
o $C_6H_4Cl_2$, Orthodichlorbenzene,
m$C_6H_4(NO_2)_2$, Metadinitrobenzene,
p $C_6H_4ClNO_2$, Parachlornitrobenzene.

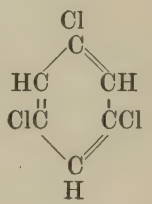
The tri-substitutions of benzene are named in the same manner :

op $C_6H_3Cl_3$ is $C_6H_3Cl_3$ 1 . 2 . 4.

There are also three tri-substitutions of benzene when the three entering atoms, or atomic groups, are the same :







or : 1) C_6H_3 {1 Cl, 2 Cl, 3 Cl} 2) C_6H_3 {1 Cl, 2 Cl, 4 Cl} 3) C_6H_3 {1 Cl, 3 Cl, 5 Cl}

1 . 2 . 5 is the same as 1 . 2 . 4, and 1 . 2 . 6 = 1 . 2 . 3.

If the substituting atoms or groups are different, the number of isomers is much greater. If two of them are different, there will be six isomers; if all three are different, there will be ten isomers.

The number of isomers of tetra-substitutions, when all the atoms or groups are the same, is the same as in the case of di-substitutions. If the substituting elements, or groups, differ among themselves, the number of isomers will be greater than in the case of tri-substitutions. When only one H remains unsubstituted, *i.e.* when five of the H's are substituted by the same atoms or groups, only one compound is possible. If the atoms differ among themselves, there will be a greater number of isomers.

If one or more H's of benzene are replaced by CH_3, the substitution of Cl, etc., can take place either in the benzene-nucleus, or in the methyl-group (*side-chain*) giving rise to a new form of isomerism :

$$C_6H_4\begin{cases}Cl\\CH_3\end{cases}, \text{ or } C_6H_5{}^-CH_2Cl.$$

The striking differences between these two kinds of compounds will be explained later on.

If an H of the benzene is replaced by an ethyl instead of a methyl, we shall have still a new form of isomerism, for the ethyl-benzene is isomeric with each of the three di-methyl-benzenes :

$$C_6H_4\begin{cases}1\,CH_3\\2\,CH_3\end{cases};\quad C_6H_4\begin{cases}1\,CH_3\\3\,CH_3\end{cases};\quad C_6H_4\begin{cases}1\,CH_3\\4\,CH_3\end{cases};$$
$$C_6H_5{}^-C_2H_5.$$

Benzene, *Benzol,* C_6H_6. Nearly all organic bodies yield benzene at a red heat. It is formed, therefore, in the manufacture of illuminating gas, and is contained in the tar, from which it is obtained by distillation. It is also produced when a mixture of the first carboxyl derivative of it, benzoic acid, $C_6H_5{}^-COOH$, and an alkali are submitted to dry distillation.

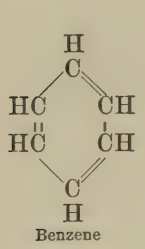
This reaction is exactly analogous to the formation of methane from acetic acid :

$$\underset{\text{Sodium acetate}}{CH_3{}^{-}COONa} + NaHO = CH_4 + Na_2CO_3$$

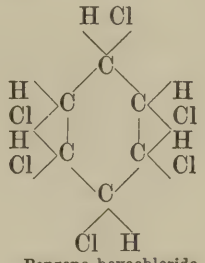
$$\underset{\text{Sodium benzoate}}{C_6H_5{}^{-}COONa} + NaHO = C_6H_6 + Na_2CO_3.$$

Benzene (formerly also called benzine)* is a colorless liquid boiling at 80.5°. It is strongly refractive, and has a peculiar aromatic odor and taste. Its sp. gr. is 0.88. It is easily inflammable, burning with a strongly luminous, smoky flame. At 0° it solidifies to a crystalline mass, which fuses at 8°. It is insoluble in water, miscible with alcohol and ether, and dissolves sulphur, phosphorus, iodine, fats, resins, etc. It is used in technology as the starting-out point for the production of aniline and the coloring matters derived from it. If chlorine is passed through benzene, addition-products are formed, viz.: $C_6H_6Cl_2$, $C_6H_6Cl_4$, and finally, $C_6H_6Cl_6$.

The double bindings are successively dissolved :



Benzene



Benzene hexachloride

If molybdenum pentachloride or iodine is added to the benzene, the chlorine substitution-products are formed. In the

* The term "benzine" is now used to designate the distillates of petroleum going over between 70°–100°, and which consist of a mixture of hydrocarbons of the C_nH_{2n+2}, and C_nH_{2n} series, principally of C_6H_{14}, C_6H_{12}, C_7H_{16}, C_7H_{14}, etc.

former case, chlorine tri-iodide is formed, which causes the substitution; in the latter case the molybdenum chloride gives up a part of its chlorine to the benzene, and is regenerated by the chlorine, which is being continually introduced. The first substitution product is

Monochlorbenzene, C_6H_5Cl. This product is obtained when the action of the chlorine has not been of too great duration.

Chlorbenzene can also be obtained by the action of phosphorus chloride on the hydroxyl-derivative of benzene (phenol):

$$3\,C_6H_5(OH) + PCl_3 = 3\,C_6H_5Cl + P(OH)_3.$$

It is a colorless liquid boiling at 132°. Like most of the chlorides of the aromatic compounds, it differs from the chlorides of the fatty compounds in its chlorine being very strongly bound, and hence not easily substituted. Neither alcoholic potassa, silver salts, nor ammonia react with it. Nascent hydrogen converts it back into benzene. A mixture of chlorbenzene and methyl iodide, treated with sodium, yields *methylbenzene:*

$$C_6H_5Cl + CH_3I + Na_2 = C_6H_5{}^-CH_3 + NaCl + NaI.$$

In the same manner chlorbenzene when digested with sodium gives *diphenyl:* *

$$C_6H_5Cl + C_6H_5Cl + Na_2 = C_6H_5{}^-C_6H_5 + 2\,NaCl.$$

We shall meet this reaction frequently.

Diphenyl, $C_6H_5{}^-C_6H_5$, or $C_{12}H_{10}$, crystallizes in colorless leaflets fusing at 70° and distilling at 254°. Like benzene, it is the starting-out point for a vast number of derivatives.

Dichlorbenzene, $C_6H_4Cl_2$. All three are known. Two of them, the para-compound (1 . 4) principally, and the ortho-

* The benzene rest, $C_6H_5{}^-$, is called *phenyl.*

compound in lesser amounts, are formed by the continued action of chlorine on benzene in the presence of iodine.

o $C_6H_4Cl_2$ boils at 179°; m $C_6H_4Cl_2$ boils at 172°; p $C_6H_4Cl_2$ is solid, and fuses at 54° and boils at 173°.

Trichlorbenzene, $C_6H_3Cl_3$, is also known in all three modifications.

The orthopara (1 . 2 . 4) is formed by the continued action of chlorine on benzene. It fuses at 17° and boils at 213°. The second, metameta (1 . 3 . 5), is obtained by the decomposition of trichloraniline. It fuses at 63° and boils at 208°. The third, orthometa (1 . 2 . 3), fuses at 53°, and boils at 218°.

Tetrachlorbenzene, $C_6H_2Cl_4$, is known in its three modifications.

1) (1 . 2 . 4 . 5) is produced by the action of chlorine on benzene. Crystals fusing at 138° and boiling at 246°.

2) (1 . 2 . 4 . 6) needles fusing at 51° and boiling at 246°.

3) (1 . 2 . 3 . 4) crystals fusing at 46° and boiling at 254°.

Pentachlorbenzene, C_6HCl_5. Needles fusing at 85° and boiling at 270°.

Perchlorbenzene, C_6Cl_6, is the final product of the action of chlorine on benzene. It fuses at 226° and boils at 332°.

Monobrombenzene, C_6H_5Br, is formed when bromine is allowed to act on benzene for some time (14 days). It is a liquid boiling at 154°.

At a higher temperature substitution-products richer in bromine are formed. Most of them are solid.

All three of the *dibrombenzenes,* $C_6H_4Br_2$, are known. Two of them (1 . 2, b. p. 224°, and 1 . 3, b. p. 219°), are liquids. The third (1 . 4) is solid, fusing at 89° and boiling at 219°.

Tribrombenzenes, $C_6H_3Br_3$. 1) 1 . 2 . 4 fuses at 44° and boils at 276°. 2) 1 . 2 . 3 fuses at 87°. 3) 1 . 3 . 5 fuses at 119° and boils at 278°.

Tetrabrombenzenes, $C_6H_2Br_4$. 1) 1 . 2 . 3 . 5 fuses at 99°. 2) 1 . 2 . 4 . 5 fuses at 140°.

Pentabrombenzene, C_6HBr_5, fuses above 240°.
Hexabrombenzene, C_6Br_6, fuses above 300°.

Mono-iodobenzene, C_6H_5I, and substitution-products richer in iodine are formed when iodine is allowed to act on benzene in the presence of iodic acid. C_6H_5I is liquid (b. p. 185°). The others are solid.

Chlorbrombenzenes, C_6H_4ClBr, etc., are also known.

Nitrobenzene, $C_6H_5{}^-NO_2$. If benzene is added to fuming nitric acid as long as it dissolves, and the solution then poured into water, nitrobenzene is precipitated in the form of a heavy, light-yellow oil. It has a pleasant odor, resembling that of bitter almonds. It boils at 205°, and is insoluble in water and soluble in alcohol and ether. It is used in perfumery under the name of "oil of mirbane," and also for the production of aniline.

Reducing agents convert the nitro-group into the amido-group. Nitrobenzene is thereby converted into *amidobenzene*, or *aniline*.

$$C_6H_5{}^-NO_2 + 3\,H_2 = C_6H_5{}^-NH_2 + 2\,H_2O.$$

Dinitrobenzene, $C_6H_4(NO_2)_2$, is formed, when benzene is added to a mixture of nitric and sulphuric acids.

The ortho-compound fuses at 118°, the meta- at 90°, and the para- at 172°.

Reducing agents convert it first into nitro-amidobenzene, or nitraniline, $C_6H_4(NO_2)NH_2$, and then into the di-amidobenzene, $C_6H_4(NH_2)_2$.

Substitution-products which contain chlorine, bromine, and the nitro-group are also known.

Benzenesulphonic acid, $C_6H_5SO_3H$, is produced by digesting benzene with concentrated sulphuric acid:

$$C_6H_6 + H_2SO_4 = C_6H_5{}^-SO_3H + H_2O.$$

It forms deliquescent crystals containing $1\frac{1}{2}$ molecules of water. It is a monobasic acid, and forms crystalline salts with bases. Nitric acid nitrates it. Phosphorus pentachloride converts it into *benzenesulphochloride*, $C_6H_5{}^-SO_3Cl$, which, by the action of ammonia, is converted into *benzenesulphamide*, $C_6H_5{}^-SO_3(NH_2)$, (f. p. 153°), by the action of zinc dust, into *zinc benzenesulphinate*, $Zn(C_6H_5{}^-SO_2)_2$, and by zinc and HCl into $C_6H_5{}^-SH$, *phenolsulphydrate*, corrresponding to the mercaptan of the fatty series.

As we have already seen (p. 199), the sulphur in sulphonic acids is bound directly to the carbon. Hence the reduction takes place in a manner analogous to that of the nitro-compounds :

$C_6H_5{}^-NO_2$ is reduced to $C_6H_5{}^-NH_2$
$C_6H_5{}^-SO_3H$ " " $C_6H_5{}^-SH$

On heating benzene with fuming sulphuric acid, there is formed,

Benzene-disulphonic Acid, $C_6H_4(SO_3H)_2$. It is a dibasic acid. The three modifications are known.

Benzenetrisulphonic acid has also been obtained.

By heating benzene with sulphuric anhydride, we obtain *Sulphobenzide, Diphenylsulphone*, $C_6H_5{}^-SO_2{}^-C_6H_5$, which fuses at 128°. It is no longer an acid, as both of the hydroxyls of the sulphuric acid are replaced by the group C_6H_5.

Phenol, Carbolic Acid, *Hydroxylbenzene*, $C_6H_5{}^-OH$. Phenol is the chief constituent of heavy coal-tar, and is produced on a large scale. It crystallizes in long colorless needles fusing at 42° and boiling at 182°. It possesses an unpleasant and clinging odor, and a burning caustic taste. Its sp. gr. is 1.065. On exposure to the air it gradually turns red. A small amount of water prevents it from crystallizing. It is soluble in 15 parts of water. It is very poisonous, coagulates albumen, and produces blisters on the skin. Solutions of ferric salts are

colored intensely violet by it. A slip of pine-wood moistened with chlorhydric acid, and then dipped in phenol and exposed to the sunlight, becomes blue. Bromine produces, even in dilute solutions, a white precipitate of tribromphenol. It is used in medicine, and as a disinfecting and antiseptic agent, and also in the production of numerous colors.

The hydroxyl-derivatives of the benzene series are called *phenols*, as they differ considerably from the alcohols of the fat series, although they are really a class of tertiary alcohols. They possess quite strong acid properties, and unite easily with metals to form species of salts. Phenol dissolves in sodium hydroxide solution, forming sodium phenoxide or phenylate, C_6H_5ONa. It dissolves lead oxide, producing lead phenoxide, $(C_6H_5O)_2Pb$. If Cl, Br, I, or NO_2, is present besides the OH, the resulting compounds have completely acid properties and act as true acids.

By treating phenols with phosphorus chloride, or bromide, the OH is replaced by Cl, Br, etc.

They are not oxidized to aldehydes, ketones, or acids, since outside of the OH there is no hydrogen united to the carbon atom (tertiary alcohols).

They unite with acid rests, forming compounds which correspond to the esters. On heating with zinc dust, the phenols are converted back into hydrocarbons by inverse substitution:

$$C_6H_5OH + Zn = C_6H_6 + ZnO.$$

Phenol can be produced from benzene in two ways. 1) By converting the benzene into benzenesulphonic acid, $C_6H_5{}^-SO_3H$, and fusing this with potassium hydroxide :

$$C_6H_5{}^-SO_3H + 2\,KOH = C_6H_5(OH) + K_2SO_3 + H_2O.$$

2) By converting the benzene into nitrobenzene, reducing this to amidobenzene, $C_6H_5{}^-NH_2$, and the amidobenzene into the so-called diazobenzene, which is decomposed by water into phenol.

The hydrogen atoms of phenol can be substituted in the same manner as those of benzene.

There are obtained by the action of chlorine :

Monochlorphenol, C_6H_4ClOH (1 . 2, b. p. 176° ; 1 . 3, b. p. 214° ; 1 . 4, b. p. 217°).

Dichlorphenol, $C_6H_3Cl_2OH$ (1 . 2 . 4, f. p. 43°, b. p. 214°).

Trichlorphenol, $C_6H_2Cl_3OH$ (f. p. 68°, b. p. 244°).

By leading chlorine through phenol in the presence of iodine, *i.e.* by the action of iodine chloride, we obtain *perchlorphenol*, C_6Cl_5OH, fusing at 187°.

Bromine and iodine act in a similar manner.

By the action of nitric acid, nitro-derivatives are obtained from phenol up to the third substitution :

$C_6H_4(NO_2)OH$, *Mononitrophenol*, all three modifications are known.

$C_6H_3(NO_2)_2OH$, *Dinitrophenol*, four modifications are known.

$C_6H_2(NO_2)_3OH$, *Trinitrophenol*, two modifications are known.

Nitrophenols, $C_6H_4(NO_2)OH$. 1 . 2, yellow prisms fusing at 45° and boiling at 214°. 1 . 3, colorless crystals fusing at 96°. 1 . 4, colorless needles fusing at 115°.

Dinitrophenols, $C_6H_3(NO_2)_2OH$: α, leaflets fusing at 114° ; β, needles fusing at 64° ; γ, bright yellow needles fusing at 104° ; δ, colorless prisms fusing at 141°.

Trinitrophenol, **Picric Acid**, $C_6H_2(NO_2)_3OH$. (1 . 2 . 4 . 6).*

Picric acid is formed by the action of nitric acid on various organic compounds (indigo, Peruvian balsam, silk, wool, etc.), most easily, however, from phenol. It crystallizes in light yellow, glittering, odorless leaflets, which taste intensely bitter. They are soluble in water, fuse at 122°, and explode on rapid heating. Weak reducing agents (ammonium sulphide) convert it into *dinitroamidophenol*, or *picramic acid*, stronger

* Substitution-derivatives of benzene and its analogues are termed *symmetrical* when the intervals between the substituting elements or groups are equal. The following derivatives are symmetrical : 1 . 4 ; 1 . 3 . 5 ; 2 . 4 . 6, etc.

reducing agents (tin and chlorhydric acid), into *triamidophenol*, or *picramine*.

Potassium picrate, $C_6H_2(NO_2)_3OK$, crystallizes in yellow needles, which explode violently by heating or percussion.

Picric acid is used as a yellow dye for silk and wool.

When heated with potassium cyanide, picric acid gives a deep violet-red liquid, which contains the potassium salt of *isopurpuric acid*, $C_8H_5N_5O_6$:

$$\underset{\text{Picric acid}}{C_6H_2(NO_2)_3OH} + 3\,KCN + 3H_2O = \underset{\substack{\text{Potassium}\\ \text{isopurpurate}}}{C_8H_4KN_5O_6} + CO_2 + NH_3 + 2\,KHO.$$

Isopicric acid, $C_6H_2(NO_2)_3OH$, (1 . 3 . 4 . 5) is formed by the action of fuming nitric acid on m-nitrophenol. Bright yellow prisms fusing at 170°.

There are also derivatives of phenol which contain chlorine, bromine, or iodine and the nitro-group, *e. g.*,

Monochlornitrophenol, $C_6H_3Cl(NO_2)(OH)$.

Phenolmethyl Ether, *Anisoïl*, $C_6H_5{-}O{-}CH_3$, is formed by the action of methyl iodide on potassium phenoxide:

$$C_6H_5OK + CH_3I = C_6H_5O{-}CH_3 + KI,$$

or by the distillation of potassium phenoxide with potassium methylsulphate:

$$C_6H_5OK + CH_3{-}KSO_4 = C_6H_5O{-}CH_3 + K_2SO_4.$$

Both of the reactions are analogous to those of the formation of the ethers of the fat-compounds.

It is a colorless liquid with a pleasant odor, boiling at 152°, and insoluble in water. The benzene nucleus is chlorinated, etc., by the action of chlorine, bromine, or iodine. Nitric acid nitrates it. Mono-, di-, and tribromanisoïl, and mono-, di-, and trinitroanisoïl are known.

Phenylethyl Ether, *Phenetoïl*, $C_6H_5{-}O{-}C_2H_5$, is produced in an analogous manner. It boils at 172°.

Phenyl Ether, $C_6H_5{-}O{-}C_6H_5$, is formed by the dry dis-

tillation of copper benzoate. It is a solid mass with a pleasant odor, fusing at 28° and boiling at 246°.

Phenol-sulphonic Acid, $C_6H_4(OH)SO_3H$, is formed in two modifications (1.2 and 1.4) by mixing phenol with concentrated sulphuric acid. Both are monobasic acids and yield finely crystallizable salts.

One of the principal salts is the zinc phenolsulphonate:

$$(C_6H_3SO_4)_2Zn + 7\,H_2O,$$

which is obtained by dissolving zinc oxide in the acid. It crystallizes in colorless, rhombic columns, easily soluble in water and alcohol. It is used as a caustic and disinfectant.

If phenol is heated with fuming sulphuric acid, *phenol-disulphonic acid,* $C_6H_3(OH)(SO_3H)_2$, is produced. It is a dibasic acid.

If the action takes place under pressure, *phenol-trisulphonic acid,* $C_6H_2(OH)(SO_3H)_3$, is obtained. It is a tribasic acid.

By digesting phenol with phosphorus pentasulphide, we obtain

Phenylsulphydrate, Phenyl Mercaptan, $C_6H_5{}^-SH$:

$$5\,C_6H_5{}^-OH + P_2S_5 = 5\,C_6H_5{}^-SH + P_2O_5.$$

It is a colorless oil with a repulsive odor, boiling at 166°, and insoluble in water. It can also be obtained by the reduction of benzenesulphonic acid. The oxygen of the air oxidizes it into *phenyl disulphide,* $(C_6H_5)_2S_2$.

$$2\,C_6H_5(SH) + O = (C_6H_5)_2S_2 + H_2O.$$

Phenylsulphide, $(C_6H_5)_2S$, is also known.

The analogous bodies of the fat-series have already been mentioned:

Ethyl mercaptan, $C_2H_5{}^-SH$,
Ethyl sulphide, $C_2H_5{}^-S{}^-C_2H_5$,
Ethyl disulphide, $C_2H_5{}^-S{}^-S{}^-C_2H_5$,
Phenyl sulphydrate, $C_6H_5{}^-SH$
Phenyl sulphide, $C_6H_5{}^-S{}^-C_6H_5$,
Phenyl disulphide, $C_6H_5{}^-S{}^-S{}^-C_6H_5$.

(See p. 102.)

All three of the hydroxyl derivatives of benzene are known. They are called catechol, resorcinol and quinol.

Catechol, Pyrocatechin, $C_6H_4(OH)_2$ (ortho-compound), is produced by heating catechu rapidly. It forms quadratic columns fusing at 104°, and boiling at 245°. Ferric chloride colors its aqueous solution green.

A monomethyl-ether of catechol, *guaiacol,* $C_6H_4(OH)(OCH_3)$, is formed by the dry distillation of guaiacum resin, and exists in beech-wood tar. It is a colorless liquid boiling at 200°.

Resorcinol, Resorcin, $C_6H_4(OH)_2$ (meta-compound), is obtained by fusing galbanum-resin with potassium hydroxide. It crystallizes in tablets fusing at 118° and boiling at 276.5°. On exposure to the air it turns red. Ferric chloride solution colors it deep-violet.

Resorcinol yields a trinitro-derivative, which stands in the same relation to resorcinol as picric acid to phenol.

Trinitroresorcinol, Styphnic Acid, $C_6H(NO_2)_3(OH)_2$. It is produced by the nitrition of resorcinol, and also by the action of cold nitric acid on numerous resins (galbanum, gum-ammoniac, etc.). It crystallizes in yellow prisms fusing at 176° and exploding by rapid heating. It is difficultly soluble in water, and behaves like a strong dibasic acid. It is used as a yellow dye.

Quinol, Hydroquinone, $C_6H_4(OH)_2$ (para-compound). It is made by leading sulphurous acid through quinone, $C_6H_4O_2$:

$$C_6H_4O_2 + H_2 = C_6H_6O_2 = C_6H_4(OH)_2.$$

Rhombic columns soluble in water. It fuses at 169° and sublimes by careful heating. It is converted into quinone by the oxygen of the air and by all oxidizing agents.

Quinone, $C_6H_4O_2$. The two following formulas have been proposed for quinone :



In the former case they would be double ketones.

Quinone is formed by the oxidation of quinol and all bodies which contain quinol. It is made by the oxidation of aniline with chromic acid. It forms golden-yellow crystals fusing at 116°, and possessing a piercing odor which irritates the eyes, and causes weeping. It is slightly soluble in cold water, easily in hot, and is volatile with steam. It is poisonous, and colors the skin brown. Oxidizing agents decompose it entirely forming oxalic acid. Reducing agents convert it into quinol.

Chlorine converts it into chlorinated quinones. The following are known :

Monochlorquinone, $C_6H_3ClO_2$,
Dichlorquinone, $C_6H_2Cl_2O_2$,
Trichlorquinone, $C_6HCl_3O_2$,
Tetrachlorquinone, $C_6Cl_4O_2$.

Tetrachlorquinone, or *Chloranile*, $C_6Cl_4O_2$, is formed by the action of $KClO_3$, on various aromatic compounds. It is usually made from phenol. It forms yellow scales soluble in water, difficultly soluble in alcohol, and which fuse at a high temperature. Sulphurous acid converts all chlorinated quinones into chlorinated quinols.

Two atoms of chlorine in chloranile can be replaced by hydroxyls and amido-groups.

Chloranilic acid, $C_6Cl_2(OH)_2O_2$, or $C_6H_2Cl_2O_4$, is formed when chloranile is warmed with potassa.

$$C_6Cl_4O_2 + 2\,KOH = C_6Cl_2(OH)_2O_2 + 2\,KCl.$$

It forms red crystals, and is dibasic.

Chloranilamide, $C_6Cl_2(NH_2)_2O$, or $C_6H_4Cl_2N_2O_2$, is formed by the action of alcoholic ammonia on chloranile :

$$C_6Cl_4O_2 + 4\,NH_3 = C_6Cl_2(NH_2)_2O_2 + 2\,NH_4Cl.$$

Reddish-brown needles which yield ammonia and chloranilic acid when treated with potassa.

Bromine substitutions of quinone have also been obtained. They resemble the chlorinated quinones.

Quinone unites with quinol to form an intermediate product known as green hydroquinone or quinhydrol :

$$C_6H_4O_2 + C_6H_6O_2$$

It forms glittering needles which can be converted into either quinone or quinol.

Only two of the three possible trihydroxyl derivatives of benzene are known, viz., pyrogallic acid and phloroglucinol.

Pyrogallic Acid, or *Pyrogallol*, $C_6H_3(OH)_3$, or $C_6H_6O_3$, (1 . 2 . 4), is formed by heating gallic acid :

$$C_6H_2(OH)_3{}^{-}COOH = C_6H_3(OH)_3 + CO_2.$$

It forms white, glittering leaflets with a bitter taste, fusing at 115°. Although it unites with metals to form a species of salts, it has no true acid properties. It is a trihydric tertiary alcohol. Water dissolves it easily. Its aqueous solution absorbs oxygen from the air with avidity, especially when an alkali is present. It acts, therefore, strongly reducing. The final products which are formed from it by the assumptiou of oxygen, are oxalic and acetic acids. It colors ferrous salts dark blue, and ferric salts red. On heating with zinc dust, it is converted into benzene :

$$C_6H_3(OH)_3 + 3\,Zn = C_6H_6 + 3\,ZnO.$$

A solution of pyrogallol containing potassium hydroxide is used in gas analysis to remove oxygen from mixtures of gases (eudiometric analysis). Pyrogallol is also used in photography.

Phloroglucinol, or *Phlorglucin*, $C_6H_3(OH)_3$, or $C_6H_6O_3$, is obtained by the decomposition of complicated bodies. It forms large, colorless crystals with a sweet taste, which contain two molecules of water. It fuses at 220° and reduces

alkaline cupric solutions like dextrose. A bromine and nitro-derivative of it are known.

There are no further hydroxyl substitutions of benzene known.

Among the amido-derivatives of benzene, amidobenzene is the most important, partly because an enormous number of compounds are derived from it, and partly because it serves as the starting-out point for the production of a series of dyes which are commercially very important.

Amidobenzene, **Aniline**, $C_6H_5{}^-NH_2$, or C_6H_7N. Like all amido-derivatives of the aromatic series, aniline is formed by the reduction of a corresponding nitro-compound. The reducing agents which are generally used for the reduction of nitro-compounds, and nitro-benzene in particular, are: 1). Alcoholic ammonium sulphide, in which the hydrogen sulphide is the reducing agent, and sulphur is set free. 2). Zinc and chlorhydric acid. 3). Tin and chlorhydric acid. 4). Iron filings and acetic acid. 5). And, finally, zinc dust and water. The last four act by setting free hydrogen.

Aniline is formed also by the dry distillation of many aromatic compounds (indigo) and also by the ignition of bones and coal (it exists in coal tar). Aniline is made commercially by the reduction of nitrobenzene with iron filings and acetic acid, or zinc dust and water:

$$C_6H_5{}^-NO_2 + 3\,H_2 = C_6H_5{}^-NH_2 + 2\,H_2O.$$

Aniline cannot be obtained by the digestion of chlorbenzene with alcoholic ammonia, as ethylamine is formed from ethyl chloride.

Aniline is a light-yellow, strongly refractive liquid with a peculiar odor. It is somewhat heavier than water (sp. gr. 1.02) and boils at 185°. On long standing it becomes colored brown by the action of the air and light.

The minutest trace of aniline can be detected by the deep violet color which is produced when it is brought into contact

with calcium hypochlorite (chloride of lime). The color passes quickly into a dirty red.

The aniline colors will be mentioned later on.

Aniline has basic properties and unites with acids to form salts, of which the hydrochloride, oxalate and nitrate are the most important, *e. g.*, $C_6H_5{}^-NH_2.HCl$. It unites also with many salts to form peculiar double compounds, viz.:

$$ZnCl_2.2\,C_6H_7N.$$

Aniline yields three kinds of derivatives depending on whether the substitution takes place in the hydrogen of the benzene nucleus, the hydrogen of the amido-group, or in both.

Chlorine, bromine and iodine form chlor-, brom-, and iodo-anilines, concentrated sulphuric acid gives a sulphonic acid, and nitric acid a nitro-derivative. All of these substitutions take place in the benzene nucleus.

The chlorine, etc., derivatives of the fatty compounds produce derivatives of aniline in which the substitution occurs in the amido-group.

If aniline is digested with methyl iodide, ethyl iodide, etc., we obtain methylaniline, dimethylaniline, ethylaniline, diethylaniline (secondary and tertiary anilines).

$$C_6H_5{}^-NH_2 + CH_3I = C_6H_5{}^-NH(CH_3).HI.$$
$$C_6H_5{}^-NH(CH_3) + CH_3I = C_6H_5{}^-N(CH_3)_2.HI.$$

The ammonium compounds are also known, viz.:

$$C_6H_5{}^-N(CH_3)_3I \quad \text{and} \quad C_6H_5{}^-N(CH_3)_3OH.$$

As the alcohols react on aniline hydrochloride at an elevated temperature, they may be used instead of the iodides to produce the methylated, etc., anilines.

$$C_6H_5{}^-NH_2.HCl + CH_3OH = C_6H_5NH(CH_3).HCl + H_2O$$
$$C_6H_5{}^-NH_2.HCl + 2\,CH_3OH = C_6H_5N(CH_3)_2.HCl + 2\,H_2O.$$

The anilines in which one or both of the amido-hydrogen atoms are replaced by hydrocarbon rests, are liquids resembling aniline, and, as they possess basic properties, form crystalline salts with acids.

If the secondary and tertiary anilines are heated for some time in closed vessels at 300°, they are converted into primary bases by atomic migration, the methyl of the amido-group exchanging with a hydrogen atom of the benzene nucleus:

$$\underset{\text{Methylaniline}}{C_6H_5NHCH_3} \quad \text{gives} \quad \underset{\text{Toluidine}}{C_6H_4(CH_3)NH_2}$$

$$\underset{\text{Dimethylaniline}}{C_6H_5N(CH_3)_2} \quad \text{gives} \quad \underset{\text{Xylidine}}{C_6H_3(CH_3)_2NH_2}.$$

In this manner all the hydrogen atoms in aniline have been successively replaced by hydrocarbon rests.

In the same manner that both H's of the amido-group of aniline can be successively replaced by mono-valent hydrocarbon rests, the substitutions can be effected by di-valent hydrocarbon rests. In this case, however, the di-valent rest may replace one H in two molecules of the amide, or two H's in one molecule.

$$\left.\begin{matrix}(C_6H_5\text{-}NH)\\(C_6H_5\text{-}NH)\end{matrix}\right\rangle C_2H_4 \quad \text{or} \quad \begin{matrix}CH_2\text{-}NH\text{-}C_6H_5\\|\\CH_2\text{-}NH\text{-}C_6H_5\end{matrix} \quad \text{Ethylenediphenyldiamine,}$$

$$\left.\begin{matrix}(C_6H_5)_2\\(C_2H_4)_2\end{matrix}\right\} N_2 \quad \text{or} \quad \begin{matrix}CH_2\text{-}N(C_6H_5)\text{-}CH_2\\|\\CH_2\text{-}N(C_6H_5)\text{-}CH_2\end{matrix} \quad \text{Di-ethylenediphenyldiamine, and}$$

$$C_6H_5\text{-}N{=}(C_2H_4) \quad \text{or} \quad \begin{matrix}CH_2\\|\\CH_2\end{matrix}\rangle N\text{-}C_6H_5 \quad \text{Ethylenephenylamine.}$$

In the first case two H's in two aniline molecules are replaced by one ethylene, in the second case, four H's in two aniline molecules are replaced by two ethylenes, in the third case, two H's in one molecule of aniline are replaced by one ethylene. They are all formed by the action of ethylene bromide on aniline.

The group $CH_3\text{-}CH{=}$, *ethylidene*, which is isomeric with ethylene $CH_2{=}CH_2$, can also be introduced into aniline, producing:

$$\left.\begin{matrix}(C_6H_5)_2\\C_2H_4\\H_2\end{matrix}\right\} N_2 \quad \text{or} \quad CH_3\text{-}CH\langle\begin{matrix}NH\text{-}C_6H_5\\NH\text{-}C_6H_5\end{matrix} \quad \text{Ethylidenediphenyldiamine.}$$

$$\left.\begin{matrix}(C_6H_5)_2\\(C_2H_4)_2\end{matrix}\right\}N_2 \quad \text{or} \quad CH_3{-}CH\begin{matrix}N(C_6H_5)\\N(C_6H_5)\end{matrix}CH{-}CH_3$$

Di-ethylidene-diphenyldiamine. They are formed by the action of aldehyde on aniline. The isomerism between these two series is clearly shown by the constitutional formulas. In the ethylene compound, both of the two carbon atoms of the ethylene are united to N, while in the other series, only one carbon atom is in combination with the N.

Tri-valent hydrocarbon rests can also be introduced into aniline, as for instance, CH≡, which may be introduced into aniline by the action of chloroform. We have, for example :

$$\left.\begin{matrix}CH\\(C_6H_5)_2\\H\end{matrix}\right\}N_2 \quad \text{or} \quad CH\begin{matrix}N{-}C_6H_5\\NH{-}C_6H_5\end{matrix} \quad \text{Methenyldiphenyldiamine,}$$

also

$$\left.\begin{matrix}C_2H_3\\(C_6H_5)_2\\H\end{matrix}\right\}N_2 \quad \text{or} \quad CH_3{-}C\begin{matrix}N{-}C_6H_5\\NH{-}C_6H_5\end{matrix} \quad \text{Ethenyldiphenyldiamine, etc.}$$

As these bodies contain one or more aniline rests, they are capable of combining with one or more molecules of acid to form salts.

The amido-hydrogen of aniline can also be substituted by acid rests forming bodies called *anilides.*

Formanilide, $C_6H_5{-}NH(CHO)$. CHO is the mono-valent rest of formic acid. The compound is produced by heating aniline oxalate :

$$(C_6H_5NH_2)_2C_2H_2O_4 = C_6H_5NH(CHO) + C_6H_5NH_2 + CO_2 + H_2O.$$

Acetanilide, $C_6H_5{-}NH(C_2H_3O)$, is formed by the action of acetyl chloride on aniline, or by boiling aniline with glacial acetic acid, or acetic anhydride. It fuses at 112° and boils at 295°.

The substitution of an acid rest may also be effected by the di-valent acid rest of a di-basic acid, *e.g.* the rest of the hypothetical carbonic acid,

$$CO\begin{matrix}OH\\OH\end{matrix} \text{ by the rest } CO<$$

$C_6H_5NH\rangle CO$ *Carbanilide*
$C_6H_5NH\rangle$

$C_6H_5NH\rangle CO$ *Carbanilamide.*
$NH_2\rangle$

Both of the compounds are ureas in which one or two H's are replaced by the benzene rest. We have already seen (p. 51) that one or more hydrogen atoms in urea may be replaced by hydrocarbon rests:

$CO\langle \begin{matrix} NHC_2H_5 \\ NH_2 \end{matrix}$ Ethylurea

$CO\langle \begin{matrix} NH(C_2H_5) \\ NH(C_2H_5) \end{matrix}$ Di-ethylurea.

Hence:

$CO\langle \begin{matrix} NH(C_6H_5) \\ NH \end{matrix}$ Carbanilamide is *Phenylurea*

$CO\langle \begin{matrix} NH(C_6H_5) \\ NH(C_6H_5) \end{matrix}$ Carbanilide is *Diphenylurea.*

Corresponding to these compounds, there are sulphur compounds, which are derived from the hypothetical sulphocarbonic acid,

$CS\langle \begin{matrix} SH \\ SH \end{matrix}$

by the replacement of the SH by NHC_6H_5, the aniline-rest. They may also be considered as derived from thiurea, $CS\langle \begin{matrix} NH_2 \\ NH_2 \end{matrix}$, by the substitution of hydrogen:

$C_6H_5NH\rangle CS$, *Sulphocarbanilide, Diphenylthiurea,*
$C_6H_5NH\rangle$

$C_6H_5NH\rangle CS$, *Sulphocarbanilamide, Phenylthiurea.*
$NH_2\rangle$

Also those in which both of the atoms of amido-hydrogen in one molecule of aniline are replaced by one di-valent rest:

$C_6H_5{}^{-}N{=}CO$, *Carbanile*,
$C_6H_5{}^{-}N{=}CS$, *Sulphocarbanile*.

These two bodies are the cyanic ether, and the mustard-oil of phenyl:

$CO{=}N{}^{-}CH_3$, Methyl cyanate,
$CO{=}N{}^{-}C_6H_5$, Phenyl cyanate,
$CS{=}N{}^{-}CH_3$, Methyl-mustard-oil,
$CS{=}N{}^{-}C_6H_5$, Phenyl-mustard-oil.

A mono-valent rest of a dibasic acid can also substitute an atom of the amido-hydrogen:

$$CO\begin{matrix}NH(C_6H_5)\\OH\end{matrix}, \textit{ Carbanilic acid.}$$

We shall have occasion to study many other anilides. They are all formed either by heating the corresponding aniline salt, or by elimination of the elements of water, or hydrogen sulphide:

$$\underset{\text{Aniline acetate}}{C_6H_5NH_2 \cdot C_2H_4O} = \underset{\text{Acetanilide}}{C_6H_5NH^{-}(C_2H_3O)} + H_2O.$$

The anilides are converted back into the aniline salts *by taking up the elements of water*. Several of them are produced by particular methods which will be mentioned when we come to consider the compounds individually.

Carbanilide (*Diphenylurea*), $\begin{matrix}C_6H_5{}^{-}NH\\C_6H_5{}^{-}NH\end{matrix}\!\!>\!CO$, (f. p. 235°), and *Carbanilamide* (*Monophenylurea*), $\begin{matrix}C_6H_5{}^{-}NH\\NH_2\end{matrix}\!\!>\!CO$, (f. p. 144°), are formed when aniline is heated with urea:

$$\begin{matrix}C_6H_5NH_2\\C_6H_5NH_2\end{matrix} + \begin{matrix}NH_2\\NH_2\end{matrix}\!\!>\!CO = \begin{matrix}C_6H_5NH\\C_6H_5NH\end{matrix}\!\!>\!CO + 2\,NH_3,$$

$$C_6H_5NH_2 + \begin{matrix}NH_2\\NH_2\end{matrix}\!\!>\!CO = \begin{matrix}C_6H_5NH\\NH_2\end{matrix}\!\!>\!CO + NH_3,$$

or when potassium cyanate is boiled with aniline sulphate:

$$2\,KCON + (C_6H_5{-}NH_2)_2{-}H_2SO_4 = 2\,CO\begin{matrix}\diagup NH{-}C_6H_5\\ \diagdown NH_2\end{matrix} + KSO_4.$$

$$2\,KCON + 2\,[(C_6H_5{-}NH_2)_2{-}H_2SO_4] = 2\,CO\begin{matrix}\diagup NH{-}C_6H_5\\ \diagdown NH{-}C_6H_5\end{matrix} + K_2SO_4 + (NH_4)_2SO_4.$$

The substituted ureas are formed according to this latter reaction in the same manner as urea itself. As we have seen (p. 49), urea is formed by boiling potassium cyanate with ammonium sulphate. If aniline sulphate, *i.e.* phenylated ammonium sulphate is substituted for the ammonium sulphate, a phenylated urea is produced.

Both are solid compounds crystallizing in needles.

Carbanile (*Phenyl cyanate*, or *Phenylcyanic Ether*), $CO{=}N{-}C_6H_5$, is formed from phenyl-mustard-oil. It is a liquid boiling at 163°, and possessing a powerful odor.

Sulphocarbanilide, $\begin{matrix}C_6H_5{-}NH\\ C_6H_5{-}NH\end{matrix}\!\!\rangle CS$, is produced by the digestion of aniline with carbon disulphide:

$$\begin{matrix}C_6H_5NH_2\\ C_6H_5NH_2\end{matrix} + CS_2 = \begin{matrix}C_6H_5NH\\ C_6H_5NH\end{matrix}\!\!\rangle CS + H_2S.$$

It crystallizes in leaflets fusing at 144°. On digestion with mercuric oxide, it exchanges its sulphur for oxygen, forming carbanilide. It yields sulphocarbanile when heated with concentrated chlorhydric acid:

$$\begin{matrix}C_6H_5NH\\ C_6H_5NH\end{matrix}\!\!\rangle CS = C_6H_5NCS + C_6H_5NH_2.$$

By digestion with ammonia and litharge, the sulphur of the sulphocarbanilide is replaced by the NH-group, forming a substituted guanidine:

$\begin{matrix}C_6H_5NH\\ C_6H_5NH\end{matrix}\!\!\rangle C(NH)$, *Diphenylguanidine.*

If, however, sulphocarbanilide is digested with aniline (substituted ammonia) and litharge, the sulphur is replaced by the di-valent-group, C_6H_5N:

$\begin{matrix}C_6H_5NH\\ C_6H_5NH\end{matrix}\!\!\rangle C(NC_6H_5)$, *Triphenylguanidine.*

Sulphocarbanile, Phenyl-mustard-oil, $C_6H_5{-}N{=}CS$, is a colorless liquid with an odor resembling that of mustard-oil. It boils at 222°, and its reactions are analogous to those of the other mustard-oils.

In the same manner, anilides have been obtained containing the rests of oxalic, succinic, malic, tartaric, and other acids.

The amido-hydrogen of aniline can also be replaced by the benzene rest. Thus by heating aniline with aniline hydrochloride, we obtain :

$$\begin{matrix} C_6H_5 \\ C_6H_5 \\ H \end{matrix}\!\!\rangle N \quad \textit{Diphenylamine},$$

which fuses at 54° and boils at 310°. It possesses basic properties, and unites with acids to form salts. The *triphenylamine* $(C_6H_5)_3N$, fusing at 127°, is also known.

The hydrogen of the benzene nucleus in aniline can, of course, be easily substituted by any element, or atomic-group, which substitutes the hydrogen of benzene. A number of isomers are met with here, depending on whether the substituting atom, or group, is separated from the NH_2-group by one or two hydrogen atoms.

There are known, for instance, chlor-, brom-, iodo-, and nitranilines, aniline-sulphonic acid, di- and trichlor-, brom-, etc., anilines. Most of them exist in numerous modifications.

The amido-hydrogen of the substituted anilides can also be substituted, viz., chloracetanilide, etc.

If two hydrogen atoms of benzene be substituted by amido-groups, three isomeric compounds are formed. They are called

Di-amidobenzenes, or *Phenylenediamine*, $C_6H_4(NH_2)_2$. They are all known. They possess basic properties, and unite with two molecules of a monobasic acid, or one molecule of a

dibasic acid, to form salts. As in aniline, both the amido-hydrogen and the hydrogen of benzene-nucleus may be substituted.

α) 1 . 2, fuses at 102° and boils at 252°; β) 1 . 3, fuses at 63° and boils at 287°; γ) 1 . 4, fuses at 147° and boils at 267°.

The ortho-diamido derivatives of the hydrocarbons, on heating with organic acids, eliminate water, forming *amidines*, while with aldehydes they yield *aldehydines*, viz. :

$C_6H_4(NH_2)_2 + CH_3{-}COOH = C_6H_4\langle \overset{N}{NH} \rangle C{-}CH_3$, *Ethylenephenyl-enamidine.*

$C_6H_4(NH_2)_2 + 2\,CH_3{-}CHO = C_6H_4\langle \overset{N}{N} \rangle (CH{-}CH_3)_2$, *Phenylenaldehydine.*

Triamidobenzene, $C_6H_3(NH_2)_3$, is obtained by the reduction of dinitraniline. It fuses at 103° and boils at 33°.

Between nitrobenzene and amidobenzene, stands a series of bodies which are formed either by the partial reduction of nitrobenzene or by the oxidation of amidobenzene.

Starting out from nitrobenzene we have

$\frac{C_6H_5NO_2}{C_6H_5NO_2}$	*Nitrobenzene,*
$\left\{\begin{matrix} C_6H_5{-}N \\ C_6H_5{-}N \end{matrix}\right\rangle O$	*Azoxybenzene,*
$\left\{\begin{matrix} C_6H_5{-}N \\ \| \\ C_6H_5{-}N \end{matrix}\right.$	*Azobenzene,*
$\left\{\begin{matrix} C_6H_5{-}NH \\ \| \\ C_6H_5{-}NH \end{matrix}\right.$	*Hydrazobenzene,*
$\frac{C_6H_5{-}NH_2}{C_6H_5{-}NH_2}$	*Amidobenzene, Aniline,*

These intermediate compounds are called *Azo-compounds.**

* Nitrogen was called *azote* by Lavoisier. From this word, the prefix "azo" is derived.

The azo-compounds contain two benzene rests united to a pair of linked nitrogen atoms.

Azoxybenzene, $\begin{matrix} C_6H_5{-}N \\ | \\ C_6H_5{-}N \end{matrix}\!\!>\!O$, or $C_{12}H_{10}N_2O$, is formed by boiling nitrobenzene with alcoholic potassa. It crystallizes in yellow, glittering needles, fusing at 36°. Nitric acid converts it into nitro-compounds, which by reduction yield azobenzene and hydrazobenzene.

Azobenzene, $C_6H_5{-}N{=}N{-}C_6H_5$, or $C_{12}H_{10}N_2$, is produced by the distillation of nitrobenzene with alcoholic potassa. It crystallizes in large yellowish leaflets, fusing at 66°. With nitric acid it forms nitro-derivatives.

Hydrazobenzene, $C_6H_5{-}NH{-}NH{-}C_6H_5$, or $C_{12}H_{12}N_2$, is formed by the action of ammonium sulphide on azobenzene. It crystallizes in colorless tablets fusing at 131°. Oxidizing agents convert it back into azobenzene, reducing agents transform it into aniline. Acids convert it at once into an isomeric compound, *benzidine*, $\begin{matrix} C_6H_4{-}NH_2 \\ | \\ C_6H_4{-}NH_2 \end{matrix}$, which is also obtained from *dinitrodiphenyl*, $\begin{matrix} C_6H_4{-}NO_2 \\ | \\ C_6H_4{-}NO_2 \end{matrix}$, by reduction with ammonium sulphide. It crystallizes in glittering, silvery leaflets, which fuse at 118°, and have strong basic properties.

There is a large class of bodies whose constitution is similar to that of azobenzene, and in which the benzene rest, C_6H_5, is united to a pair of doubly-bound nitrogen atoms, $C_6H_5{-}N{=}N{-}$. They are called *diazo-compounds*. Azobenzene may be considered as a particular case in this class of compounds, in which the free bond of the nitrogen is satisfied by a benzene rest.

If nitrous acid is passed into an alcoholic solution of aniline, *diazobenzene-anilide*, or *diazo-amido-benzene*,

$$C_6H_5{-}N{=}N{-}NH{-}C_6H_5,$$

is formed at first. By continued action, or by the use of aniline nitrate, *diazobenzene nitrate* is produced :

$$C_6H_5N{=}N{-}NO_3,$$

$$2\,C_6H_5NH_2 + HNO_2 = C_6H_5{-}N{=}N{-}NHC_6H_5 + 2\,H_2O$$

$$C_6H_5NH_2\,.\,HNO_3 + HNO_2 = C_6H_5{-}N{=}N{-}NO_3 + 2\,H_2O.$$

We see, therefore, that by the action of nitrous acid both of the atoms of amido-hydrogen in aniline are replaced by an atom of nitrogen, the third bond of which remains free.

The substituted anilines, such as chloraniline, etc., also form diazo-compounds with nitrous acid.

The diazo-compounds are unstable, exploding violently on heating, or by percussion. On heating with water, nitrogen is eliminated and a phenol is produced :

$$C_6H_5N_2{-}NO_3 + H_2O = C_6H_5OH + N_2 + HNO_3.$$

On boiling with absolute alcohol, both of the nitrogen atoms are replaced by hydrogen :

$$C_6H_5N_2{-}NO_3 + C_2H_5OH = C_6H_6 + N_2 + C_2H_4O + HNO_3,$$

Or by boiling with chlor-, brom-, or iodohydric acids, both of the hydrogen atoms are replaced by an atom of chlorine, bromine, or iodine :

$$C_6H_5N_2{-}NO_3 + HCl = C_6H_5Cl + HNO_3 + N_2.$$

By means of the diazo-compounds, therefore, the nitro-group can easily be replaced by hydroxyl, chlorine, bromine, etc.

The conversion of aniline (and all aromatic amides) into diazo-compounds, and the easy decomposition of the latter, attended by evolution of nitrogen, is a phenomenon which we have already seen to be characteristic of ammonia. In the case of ammonia, however, both of these reactions take place at once. Ammonium nitrite (*i.e.*, ammonia + nitrous acid) breaks on heating into nitrogen and water :

$$NH_3 + HNO_2 = N_2 + 2\,H_2O.$$

Compare also the action of nitrous acid on amines (p. 46).

If diazobenzene nitrate is heated with hydrogen potassium sulphite, a compound, $C_6H_5N_2H_2SO_3K$, is obtained, in which the group SO_3K can be replaced by H. The resulting body is the first member of a series of compounds having the constitution, $C_6H_5{-}NH{-}NH_2$, and which are derivatives of the unknown compound, $NH_2{-}NH_2$. They possess strong basic properties, and unite directly with acids. They are called *hydrazine compounds* (compare p. 46).

Certain derivatives of diazobenzene have of late become very important as dyes. Diazo-amidobenzene, $C_6H_5{-}N{=}N{-}NH{-}C_6H_5$, in the presence of alcohol and an aniline salt, passes after a time into the isomeric *amido-azobenzene:*

$$C_6H_5{-}N{=}N{-}C_6H_5(NH_2),$$

or *aniline-yellow*. By the action of nitrous acid on meta-di-amidobenzene, *diazo-di-amido-azobenzene:*

$$(NH_2)C_6H_4{-}N{=}N{-}NH{-}C_6H_4(NH_2),$$

which is formed, passes into the isomeric *triamido-azobenzene:*

$$(NH_2)C_6H_4{-}N{=}N{-}C_6H_3(NH_2)_2,$$

or *Bismarck-brown*. The compound intermediate between aniline-yellow and Bismarck-brown, is called *chrysoïdine*. It is an orange dye. Its salts form superb crystals, having a beetle-green, metallic sheen. It is made by the action of diazobenzene chloride on metadiamidobenzene:

$$C_6H_5{-}N{=}N{-}Cl + C_6H_4(NH_2)_2 = C_6H_5{-}N{=}N{-}C_6H_3(NH_2)_2 + HCl.$$

In a similar manner, a multitude of new colors have been produced by allowing negative derivatives of diazobenzene to react on primary and secondary monamines, phenols, and phenol-sulphonic acids. Diazosulphanilic acid and dimethylaniline yield an orange dye:

$$(HSO_3)C_6H_4{-}N{=}N{-}C_6H_4{-}N(CH_3)_2.$$

Diazocumene chloride and β-naphthol-disulphonic acid give a scarlet:

$$C_6H_2(CH_3)_3{-}N{=}N{-}C_{10}H_4(OH)(HSO_3)_2.$$

These colors are remarkable for their brilliancy and fastness, as well as for their great tinctorial powers.

A more complicated class of compounds, having greater tinctorial

powers than the preceding, is obtained by diazotizing the amido-group of amido-azobenzene, and carrying out, with the substance thus produced, reactions similar to those just mentioned :

$$\underset{\text{Amido-azobenzene}}{C_6H_5{}^-N{=}N{}^-C_6H_4(NH_2)} + HNO_2 + HCl$$
$$= \underset{\text{Diazoazo-benzene chloride}}{C_6H_5{}^-N{=}N{}^-C_6H_4{}^-N{=}N{}^-Cl} + 2\,H_2O,$$

From the chloride and β-naphthol-disulphonic acid, the scarlet,

$$C_6H_5{}^-N{=}N{}^-C_6H_4{}^-N{=}N{}^-C_{10}H_4(OH)(HSO_3)_2,$$

is obtained.

In the same manner that the amido-derivatives are produced from nitrated benzenes by reduction, the nitrated phenols can be converted into the corresponding amido-compounds.

Mononitrophenol, $C_6H_4(NO_2)OH$, into
Amidophenol, $C_6H_4(NH_2)OH$,
Dinitrophenol, $C_6H_3(NO_2)_2OH$, into
Amidonitrophenol, $C_6H_3(NO_2)(NH_2)OH$, and
Diamidophenol, $C_6H_3(NH_2)_2OH$,
Trinitrophenol, $C_6H_2(NO_2)_3OH$, into
Dinitroamidophenol, $C_6H_2(NO_2)_2(NH_2)OH$,
Triamidophenol, $C_6H_2(NH_2)_3OH$.

Corresponding to the two cyanides which exist in the fat-series, and which depend on the existence of the two isomeric cyan-groups, $^-C{\equiv}N$ and $^-N{\equiv}C$, there are two cyan-derivatives of benzene, *cyanbenzene*, or *benzonitrile*, $C_6H_5{}^-CN$, and *isocyanbenzene*, $C_6H_5{}^-NC$. Cyanbenzene is produced by the distillation of benzamide (see p. 242) with phosphoric anhydride, and is hence called *benzonitrile:*

$$C_6H_5{}^-CO{}^-NH_2 = C_6H_5{}^-CN + H_2O.$$

It is also formed by heating benzoic acid with potassium sulphocyanate:

1) $\underset{\text{Benzoic acid}}{C_6H_5{}^-COOH} + \underset{\text{Potassium sulphocyanate}}{KSCN} = \underset{\text{Potassium benzoate}}{C_6H_5{}^-COOK} + \underset{\text{Sulphocyanic acid}}{HSCN},$

2) $C_6H_5{}^-COOH + HSCN = \underset{\text{Benzonitrile}}{C_6H_5{}^-CN} + H_2S + CO_2.$

On heating with alkalis, it takes up the elements of water, and is converted into carboxylbenzene (benzoic acid) and ammonia :

$$C_6H_5{}^-CN + 2\,H_2O = C_6H_5{}^-COOH + NH_3.$$

It is a colorless liquid with the odor of bitter almonds, boiling at 191. Nitric acid nitrates it.

Isocyanbenzene, $C_6H_5{}^-NC$, is obtained by digesting aniline with chloroform and potassium hydroxide :

$$C_6H_5{}^-NH_2 + CHCl_3 + KOH = C_6H_5{}^-NC + KCl + H_2O + 2\,HCl.$$

The action of the potassa is only to accelerate the reaction. Acids decompose it into aniline and formic acid with the addition of the elements of water ;

$$C_6H_5{}^-NC + 2\,H_2O = C_6H_5{}^-NH_2 + CH_2O_2.$$

It is a colorless liquid with a highly offensive odor, boiling at 160° with partial decomposition. (Compare p. 106.)

By the action of PCl_5 on benzene at a high temperature, HCl is eliminated, and the compound, $C_6H_5{}^-PCl_2$, *phosphenyl chloride*, is formed. It is oxidized by water to *phenyl-hypo-phosphorous acid*, $C_6H_5P(OH)_2$. It unites directly with chlorine to form *phosphenyl-tetrachloride*, $C_6H_5{}^-PCl_4$, which is decomposed by a small amount of water into *phenyl-oxychloride*, $C_6H_5{}^-POCl_2$, and by an excess of water into *phenylphosphinic acid* $C_6H_5{}^-PO(OH_2)$. Phenylphosphinic acid corresponds to methylphosphinic, acid (p. 68), and phosphenyl chloride to methylphosphine, except that the hydrogen of the latter is replaced by chlorine.

Phenylphosphine, $C_6H_5{}^-PH_2$, is obtained by the action of iodohydric acid gas on phosphenyl chloride.

Among the metallo-derivatives of benzene, *mercury-phenyl*, $Hg(C_6H_5)_2$, is worthy of notice. It is produced by the action of sodium amalgam on brombenzene. It fuses at 120°, and its mercury atom is easily replaced by other groups.

Toluene.

So far, we have considered only those derivatives of benzene in which the hydrogen of the benzene nucleus has been replaced by halogens, or by atomic groups containing oxygen, sulphur, or nitrogen.

We come finally to a kind of substitution of benzene by which series of aromatic compounds are built up in the same manner as in the fatty series, viz., by the substitution of the hydrogen of the benzene by hydrocarbon-rests, as methyl, or mono-valent derivatives of methane. Let us take up the first two cases, viz., $C_6H_5{}^-CH_3$, and $C_6H_5{}^-C_2H_5$.

The two great divisions of organic bodies, the fatty and the aromatic compounds, are both represented at the same time in these substances. The derivatives which are formed by the substitution of hydrogen in the benzene nucleus possess all the characteristics of the aromatic compounds, and are, in fact, true homologues of the corresponding benzene derivatives. On the other hand, the derivatives which are formed by the substitution of the hydrogen of the methyl, or ethyl, possess all the characteristic properties of the fatty compounds, and are only aromatic compounds in so far that they contain the benzene rest with its easily substitutible hydrogen atoms. By the action of chlorine on methylbenzene, a monochlorinated substitution-product is formed, in which the chlorine enters into the benzene nucleus, $C_6H_4Cl^-CH_3$, (we shall not take into account the three possible isomeric modifications of this compound). Such a chlorine derivative has all the characteristic properties of an aromatic compound; the chlorine is hardly capable of direct replacement; neither potassium hydroxide nor silver oxide transpose it into hydroxyl; nor does ammonia replace it with the amido-group. On the other hand, the compound, $C_6H_5{}^-CH_2Cl$, has also the properties of a chloride of the fatty series. The chlorine is directly replaced with ease, for

instance by hydroxyl, when potassium hydroxide, or silver oxide, acts on it, or by the amido-group when treated with ammonia. If an atom of hydrogen in the benzene nucleus is replaced by hydroxyl, a *phenol*, $C_6H_4(OH)^-CH_3$, is produced, while, if the replacement takes place in the methyl-group, an *alcohol* is formed, $C_6H_5^-CH_2(OH)$. The benzene rest, is called the *nucleus*, and the methyl-group, the *side-chain*.

Benzene-derivatives which contain side-chains, are, therefore, divided into two sharply separated groups, viz., those in which the hydrogen of the benzene nucleus has been substituted, and those in which the hydrogen of the side-chain has been substituted.

By the substitution of hydrogen rests for the hydrogen of the benzene nucleus, the following compounds are obtained:

Methylbenzene, $C_6H_5^-CH_3 = C_7H_8$

Dimethylbenzene, (3 isomers) $C_6H_4(CH_3)_2$
Ethylbenzene, $C_6H_5^-C_2H_5$ $\Big\} = C_8H_{10}$

Trimethylbenzene, (3 isomers) $C_6H_3(CH_3)_3$
Methylethylbenzene, (3 isomers) $C_6H_4\begin{cases}CH_3\\C_2H_5\end{cases}$
Propylbenzene,* (2 isomers) $C_6H_5^-C_3H_7$ $\Big\} = C_9H_{12}$

Tetramethylbenzene, (3 isomers) $C_6H_2(CH_3)_4$
Dimethylethylbenzene, (3 isomers) $C_6H_3(C_2H_5)(CH_3)_2$
Di-ethylbenzene, (3 isomers) $C_6H_4(C_2H_5)_2$
Methylpropylbenzene, (6 isomers) $C_6H_4(CH_3)(C_3H_7)$
Butylbenzene,† (4 isomers) $C_6H_5^-C_4H_9$ $\Big\} = C_{10}H_{14}$

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* $C_6H_5^-CH_2^-CH_2^-CH_3$, and $C_6H_5^-CH\langle^{CH_3}_{CH_3}$, propylbenzene and isopropylbenzene.

†1) $C_6H_5^-CH_2^-CH_2^-CH_2^-CH_3$

2) $C_6H_5^-CH_2^-CH\langle^{CH_3}_{CH_3}$

3) $C_6H_5^-CH\langle^{C_2H_5}_{CH_3}$

4) $C_6H_5^-C\langle^{CH_3}_{CH_3}_{CH_3}$

There is only one hydrocarbon of the formula C_7H_8. But of the formula C_8H_{10} there are four; of C_9H_{12}, eight; and of $C_{10}H_{14}$, nineteen. The number of isomers increases very rapidly with the rising content of carbon. The number of cases of isomerism is also very great when the hydrogen of a highly constituted hydrocarbon is substituted by chlorine, hydroxyl, etc.

But relatively few of the vast number of compounds which we see in perspective are known, and this is particularly the case in the higher series.

Methylbenzene, **Toluene,** *Toluol,* $C_6H_5{}^-CH_3$, or C_7H_8. Toluene with other methylated benzenes, as dimethyl- and trimethylbenzene, is formed, together with benzene, by exposing many organic compounds to a very high temperature. These methylated benzenes are separated from benzene and from each other by fractional distillation.

In its physical properties, toluene resembles benzene completely. It is a colorless oil with nearly the same odor as benzene. It boils at 111°, but does not become solid under 0°. It can be made from benzene artificially, by digesting a mixture of monobrombenzene and methyl iodide with sodium:

$$C_6H_5Br + CH_3I + Na_2 = C_6H_5{}^-CH_3 + NaBr + NaI.$$

This reaction is adapted to the production of any higher aromatic hydrocarbon from benzene. To produce ethylbenzene, ethyl iodide is used, and so on. Toluene can also be converted into monobromtoluene, which with methyl iodide yields dimethylbenzene.

The methyl-group of toluene is converted by oxidizing agents into carboxyl, COOH. This is the case not only when the group is methyl, but also when it is a methyl derivative of higher carbon content. Methylbenzene, $C_6H_5{}^-CH_3$, and ethylbenzene, $C_6H_5{}^-C_2H_5$, both yield the same carboxylbenzene, $C_6H_5{}^-COOH$ (benzoic acid). The oxidation of aromatic hydrocarbons affords, therefore, a reliable method of deter-

mining how many atoms of hydrogen in benzene are substituted by hydrocarbon rests. If C_8H_{10}, for instance, yields C_6H_5COOH on oxidation, it must be ethylbenzene, while if $C_6H_4(COOH)_2$ is formed, it is proved to be dimethylbenzene.

When chlorine acts on toluene in the cold, the hydrogen of the benzene nucleus is substituted ($C_6H_4Cl^-CH_3$), but if the action takes place in heated toluene, the hydrogen of the side-chain is substituted, $C_6H_5^-CH_2Cl$.

The following chlorine derivatives of toluene are known :

$C_6H_4Cl^-CH_3$ Monochlortoluene	$C_6H_3Cl_2^-CH_3$ Dichlortoluene	$C_6H_2Cl_3^-CH_3$ Trichlortoluene
$C_6HCl_4^-CH_3$ Tetrachlortoluene	$C_6Cl_5^-CH_3$ Pentachlortoluene	
$C_6H_5^-CH_2Cl$ Benzyl chloride	$C_6H_4Cl^-CH_2Cl$ Chlorbenzyl chloride	$C_6H_3Cl_2^-CH_2Cl$ Dichlorbenzyl chloride
$C_6H_2Cl_3^-CH_2Cl$ Trichlorbenzyl chloride	$C_6HCl_4^-CH_2Cl$ Tetrachlorbenzyl chloride	$C_6Cl_5^-CH_2Cl$ Pentachlorbenzyl chloride
$C_6H_5^-CHCl_2$ Benzyl dichloride	$C_6H_4Cl^-CHCl_2$ Monochlorbenzyl dichloride	$C_6H_3Cl_2^-CHCl_2$ Dichlorbenzyl dichloride
$C_6H_2Cl_3^-CHCl_2$ Trichlorbenzyl dichloride	$C_6HCl_4^-CHCl_2$ Tetrachlorbenzyl dichloride	$C_6Cl_5^-CHCl_2$ Pentachlorbenzyl dichloride
$C_6H_5^-CCl_3$ Phenylchloroform	$C_6H_4Cl^-CCl_3$ Monochlorphenylchloroform	$C_6H_3Cl_2^-CCl_3$ Dichlorphenylchloroform
$C_6H_2Cl_3^-CCl_3$ Trichlorphenylchloroform	$C_6HCl_4^-CCl_3$ Tetrachlorphenylchloroform	

Almost every one of these compounds exists in several isomeric modifications, *e.g.*, there are three isomeric monochlortoluenes. We see hence that the number of isomeric derivatives is enormous.

If chlorine is led into cooled toluene, chlorinated derivatives are obtained in which the hydrogen of the benzene nucleus is replaced. But if the toluene is boiling, the hydrogen of the methyl-group is substituted, and the substitution thus takes place in the side-chain. The extent of substitution (mono-, di-, tri-chlortoluene, etc.), depends on the duration of the action. If, however, chlorine is passed through toluene which contains iodine, so that it is really exposed to the action of ICl_3, the substitution takes place in the benzene nucleus, even when boiling.

1. a). *Monochlortoluene*, $C_6H_4Cl^-CH_3$. All three isomers are known. The ortho- and meta-compounds boil at 156°, the para at 160°.

1. b). *Benzyl Chloride*, $C_6H_5^-CH_2Cl$, is formed by leading chlorine through boiling toluene, or by the action of HCl on *benzyl alcohol*, $C_6H_5^-CH_2OH$. It is a colorless liquid boiling at 176°. On oxidation it passes into benzoic acid, $C_6H_5^-COOH$ (p. 239).

If a mixture of benzyl chloride and benzene is warmed with aluminum chloride, HCl is evolved and benzylbenzene, or diphenylmethane, $C_6H_5^-CH_2^-C_6H_5$, is obtained. It forms needles fusing at 26° and boiling at 261°. On oxidation it is converted into *benzophenone*, $C_6H_5^-CO^-C_6H_5$.

This reaction is applicable to all chlorides of the fatty compounds and those chlorides of the aromatic compounds in which the chlorine is in the side-chain. If a chloride of this kind is mixed with an aromatic hydrocarbon and treated with aluminum chloride, chlorhydric acid is eliminated, and a compound of the two organic bodies is formed, although the aluminum chloride does not take part in the reaction.

Methyl chloride and benzene with the addition of aluminum chloride, give toluene and also dimethylbenzene, trimethylbenzene, etc.

$$CH_3Cl + C_6H_6 = CH_3^-C_6H_5 + HCl\ ;$$

$$2\,CH_3Cl + C_6H_6 = C_6H_4(CH_3)_2 + 2\,HCl, \text{ etc.}$$

Chlorine gives under the same conditions with benzene, triphenylmethane, $C_6H_3(CH_3)_3$. Acetyl chloride gives with benzene, acetophenone, (methylphenylketone), $C_6H_5^-CO^-CH_3$.

2. a). *Dichlortoluene*, $C_6H_2Cl_2^-CH_3$, is formed by leading chlorine into toluene containing iodine. It boils at 196°, and on treatment with oxidizing agents is converted into dichlordracylic acid, $C_6H_3Cl_2^-COOH$.

2. b). *Monochlorbenzyl chloride*, $C_6H_4Cl^-CH_2Cl$, is obtained by leading chlorine into benzyl chloride containing iodine, or by the action of chlorine on boiling toluene. It boils at 214°. On oxidation it is converted into chlordracylic acid.

2. c). *Benzal chloride*, $C_6H_5^-CHCl_2$, is produced either by the action of chlorine on boiling toluene, or phosphorus pentachloride on benzyl aldehyde (bitter almond-oil), $C_6H_5^-CHO$. It boils at 207°, and by oxidation is converted into benzoic acid, $C_6H_5^-COOH$.

3. a). *Trichlortoluene*, $C_6H_2Cl_3{-}CH_3$, is formed by leading chlorine into toluene containing iodine. It boils at 235°, and is converted by oxidation into trichlordracylic acid, $C_6H_2Cl_3{-}COOH$.

3. b). *Dichlorbenzyl chloride*, $C_6H_3Cl_2{-}CHCl_2$, is obtained by leading chlorine into benzyl chloride containing iodine, or by leading chlorine into boiling dichlortoluene. It boils at 241°, and on oxidation passes into dichlordracylic acid, $C_6H_3Cl_2{-}COOH$.

We shall not proceed farther with the description of the chlorinated toluenes, as we have now learned the methods by which all the remaining derivatives can be produced.

According to the duration of the action of chlorine on boiling toluene, we obtain, $C_6H_5{-}CH_2Cl$, $C_6H_5{-}CHCl_2$, or $C_6H_5{-}CCl_3$. If a chlorinated toluene is employed instead of toluene, further chlorinated derivatives are produced. If monochlortoluene, $C_6H_4Cl{-}CH_3$, is used we obtain, $C_6H_4Cl{-}CH_2Cl$, $C_6H_4Cl{-}CHCl_2$, and $C_6H_4Cl{-}CCl_3$; dichlortoluene, $C_6H_3Cl_2{-}CH_3$, yields $C_6H_3Cl_2{-}CH_2Cl$, $C_6H_3Cl_2{-}CHCl_2$, $C_6H_3Cl_2{-}CCl_3$, etc. The chlorine can hence be introduced into the side-chain at will. The chlorine can be introduced into the benzene nucleus with the same ease by either cooling the toluene, or adding iodine. In this way we can obtain from toluene :

$$C_6H_4Cl{-}CH_3\ ;\ C_6H_3Cl_2{-}CH_3\ ;\ C_6H_2Cl_3{-}CH,\ \text{etc.}$$

From benzyl chloride, $C_6H_5{-}CH_2Cl$, we have :

$$C_6H_4Cl{-}CH_2Cl\ ;\ C_6H_3Cl_2{-}CH_2Cl\ ;\ C_6H_2Cl_3{-}CH_2Cl,\ \text{etc.}$$

From benzal chloride, $C_6H_5{-}CHCl_2$,

$$C_6H_4Cl{-}CHCl_2\ ;\ C_6H_3Cl_2{-}CHCl_2\ ;\ C_6H_2Cl_3{-}CHCl_2,\ \text{etc.}$$

Bromine and iodine act similarly to chlorine. As the numerous bromine and iodine derivatives resemble the chlorine compounds, we shall omit them.

The nitro-derivatives are, however, worthy of attention. According to the theory, three mononitrotoluenes are possible. All three are known. Two of them are formed by the action of nitric acid on toluene. One of them is a liquid (liquid nitrotoluene), and has the constitution, $C_6H_4\begin{cases}1\ NO_2\\2\ CH_3\end{cases}$. It boils at 223°, and is completely destroyed by boiling with chromic acid solution. Boiling dilute nitric acid, however,

converts it into orthonitrobenzoic acid, $C_6H_4 \begin{cases} 1\,NO_2 \\ 2\,COOH \end{cases}$. The other is solid at ordinary temperatures, fuses at 54° and boils at 236°. It has the constitution, $C_6H_4 \begin{cases} 1\,NO_2 \\ 4\,CH_3 \end{cases}$, and yields on oxidation nitrodracylic acid $C_6H_4 \begin{cases} 1\,NO_2 \\ 4\,COOH \end{cases}$.

The third nitrotoluene is not obtained directly by the action of nitric acid on toluene, but by an indirect method from nitroamidotoluene. (By conversion into the diazo-compound and then into the nitrotoluene). It is liquid at ordinary temperatures, solidifies when cooled, and fuses then at 16°. It boils at 231°, and has the constitution, $C_6H_4 \begin{cases} 1\,NO_2 \\ 3\,CH_3 \end{cases}$. On oxidation it yields nitrobenzoic acid, $C_6H_4 \begin{cases} 1\,NO_2 \\ 3\,COOH \end{cases}$.

The fourth nitro-derivative of toluene, in which the nitro-group is in the side-chain, $C_6H_5{-}CH_2{-}NO_2$, has not yet been obtained.

All four hydroxyl-derivatives of toluene have been produced. Those which contain the OH in the benzene nucleus are called *cresols.* When it is in the side chain, they are known as *benzyl alcohols.*

Benzyl alcohol is a true primary alcohol, and yields benzylaldehyde and benzylic or benzoic acid on oxidation :

$C_6H_4 \begin{cases} OH \\ CH_3 \end{cases}$	Cresol.
$C_6H_5\,CH_2OH$	Benzyl alcohol (like CH_3CH_2OH)
C_6H_5CHO	Benzaldehyde (like CH_3CHO)
C_6H_5COOH	Benzoic acid (like CH_3COOH).

The cresols are phenols. Two of them, the ortho- and paracresol, occur in coal-tar. The properties of all three of them resemble those of phenol. Orthocresol fuses at 31° and boils at 185° ; metacresol is liquid and boils at 201° ; paracresol fuses at 36° and boils at 199°. By the action of oxidiz-

ing agents on them, or rather on their methyl ethers, or acetic esters, the CH_3 is converted into carboxyl, while the hydroxyl remains unchanged. A body is thus obtained of the composition $C_6H_4\begin{cases}OH\\COOH\end{cases}$. These compounds have the same relation to the phenols as the glycollic acids to the alcohols, and are at once both phenols and acids. They are called *hydroxybenzoic acids.*

Benzyl Alcohol, $C_6H_5{}^-CH_2(OH)$, or C_7H_8O, is formed from benzyl chloride (which is produced by leading chlorine into boiling toluene) by digesting with potassium hydroxide :

$$C_6H_5{}^-CH_2Cl + KOH = C_6H_5{}^-CH_2(OH) + KCl,$$

and by the reduction of benzyl aldehyde :

$$C_6H_5{}^-CHO + H_2 = C_6H_5{}^-CH_2OH,$$

or by boiling benzaldehyde with alcoholic potassa :

$$2\,C_6H_5{}^-CHO + KHO = \underset{\text{Potassium benzoate}}{C_6H_5{}^-COOK} + C_6H_5{}^-CH_2OH.$$

All of these methods of formation show very distinctly the constitution of benzyl alcohol. Chlortoluene does not yield a cresol on digestion with potassium hydroxide, because the chlorine which is in the benzene nucleus is not easily substituted. On the other hand, benzyl chloride acts like a chloride of the fatty series. The conversion of benzaldehyde into benzyl alcohol by reduction is exactly analogous to the general property of the reduction of aldehydes to alcohols mentioned on page 85.

Benzyl alcohol is a colorless liquid with an aromatic odor, boiling at 207°, and insoluble in water. It is oxidized by nitric acid into benzaldehyde (bitter almond-oil). Boric anhydride converts it into benzyl ether :

$$2\,C_6H_5{}^-CH_2OH = \begin{matrix}C_6H_5{}^-CH_2\\C_6H_5{}^-CH_2\end{matrix}\!\!>O + H_2O.$$

By treating benzyl alcohol with gaseous chlorhydric acid, it is converted into benzyl chloride, $C_6H_5{}^-CH_2Cl$.

The principal esters of benzyl alcohol are :

Benzyl Acetic Ester, $C_6H_5{-}CH_2{-}O{-}C_2H_3O$, (b. p. 210°).
Benzyl Benzoic Ester, $C_6H_5{-}CH_2{-}O{-}C_7H_5O$.
Benzyl Cinnamic Ester, $C_6H_5{-}CH_2{-}O{-}C_9H_7O$ (see later).

Benzyl-benzoic ester and benzyl-cinnamic ester occur in balsams of Peru and Tolu.

Besides the three cresols, $C_6H_4\begin{cases}OH\\CH_3\end{cases}$, and benzyl alcohol, $C_6H_5{-}CH_2OH$, we have already met another body of the formula, C_7H_8O, viz. : anisoïl, $C_6H_5{-}O{-}CH_3$, the methyl ether of phenol (p. 210).

Benzaldehyde, **Bitter Almond-Oil**, $C_6H_5{-}CHO$, or C_7H_6O. Bitter almond-oil does not occur in the free state in nature, but is formed by a peculiar fermentation of a glucoside, *amygdalin*, existing in bitter almonds, by which it breaks into dextrose, cyanhydric acid and benzaldehyde :

$$C_{20}H_{27}NO_{11} + 2\,H_2O = 2\,C_6H_{12}O_6 + CNH + C_7H_6O.$$

Bitter almond-oil is obtained by distilling bitter almonds with water. It distils over with cyanhydric acid and steam, and separates as a heavy oil in the distillate. It is also formed by the decomposition of benzal chloride with sulphuric acid, and further by heating benzyl chloride with lead nitrate.

It is a colorless, strongly refractive liquid with the odor of bitter almonds. It has a burning taste, boils at 180°, and is difficultly soluble in water. It is not poisonous, although the crude bitter almond-oil, on account of its containing cyanhydric acid, is poisonous. Benzaldehyde has all the characteristic properties of an aldehyde ; it unites with acid alkali sulphites to form crystalline compounds ; oxidizing agents convert it into benzoic acid ; hydrogen sulphide converts it into benzsulphaldehyde, $C_6H_5{-}CHS$. Phosphorus pentachloride transforms it into benzal chloride, $C_6H_5{-}CHCl_2$, *i.e.*, its oxygen is replaced by 2 Cl. It is nitrated by fuming nitric acid, forming nitrobenzaldehyde, $C_6H_4(NO_2){-}CHO$.

When mixed with potassium cyanide and allowed to stand some time, it is converted into a polymeric body, *benzoïn*, $C_{14}H_{12}O_2 = 2\,C_7H_6O$, which crystallizes in colorless, odorless prisms insoluble in water, from which chlorine abstracts two H's, forming *benzil*, $C_{14}H_{10}O_2$. Benzil is converted back into benzoïn by the action of hydrogen. Alcoholic potassa changes it into *benzilic acid*, $C_{14}H_{12}O_3$:

$$C_{14}H_{10}O_2 + KOH = \underset{\text{Potassium benzilate}}{C_{14}H_{11}KO_3}.$$

The constitution of these bodies is probably :

$$\underset{\text{Benzoïn}}{C_6H_5{-}CO{-}CH(OH){-}C_6H_5} \qquad \underset{\text{Benzil}}{C_6H_5{-}CO{-}CO{-}C_6H_5}$$

$$\underset{\text{Benzilic acid}}{(C_6H_5)_2{=}C(OH){-}CO_2H}.$$

Benzaldehyde is converted into its pinacone (p. 113), by reduction with sodium amalgam, or zinc and chlorhydric acid, the formula of this body is : $C_{14}H_{14}O_2 = C_6H_5{-}CH(OH){-}CH(OH){-}C_6H_5$, *hydrobenzoïn*. It forms tablets fusing at 134°. On oxidation, it is converted into benzoïn and benzil, and finally into benzoic acid. Like all pinacones, hydrobenzoïn splits out water easily and passes into the pinacoline, $C_{14}H_{12}O$ (f. p. 131°). On the other hand, benzoïn forms by reduction with zinc and chlorhydric acid a compound, $C_{14}H_{12}O$, *desoxybenzoïn* (*phenylbenzylketone*) ·

$$C_6H_5{-}CO{-}CH_2{-}C_6H_5.$$

There is also formed by the reduction of benzaldehyde an isomeric compound, $C_{14}H_{14}O_2$, *isohydrobenzoïn*, which also splits out water easily and is converted into $C_{14}H_{12}O$, (f. p. 102°).

Benzaldehyde is converted by the action of ammonia into *hydrobenzamide*, $C_{21}H_{18}N_2$, which forms octahedrons fusing at 110°. This body, on boiling with alkalis, falls into isomeric and strongly basic *amarine* (prisms fusing at 100°), and by distillation, into another isomeric compound, *lophine*, $C_{21}H_{18}N_2$, which forms needles fusing at 270°.

Benzaldehyde also unites with cyanhydric acid forming the nitrile of phenylglycollic acid, $C_6H_5{-}CH(OH){-}CN$, which with ammonia yields easily the nitrile of phenylamidoacetic acid, $C_6H_5{-}CH(NH_2){-}CN$. The nitriles are easily converted into *phenylglycollic acid :*

$$C_6H_5{-}CH(OH){-}COOH,$$

and *phenylamidoacetic acid*, $C_6H_5{-}CH(NH_2)COOH$, by boiling with chlorhydric acid.

Sodium eliminates the oxygen from benzaldehyde, and the two rests free from oxygen unite, forming *stilbene:*

$$C_{14}H_{12} = C_6H_5{-}CH{=}CH{-}C_6H_5,$$

which is a molecule of ethylene in which two H's are replaced by two benzene rests (diphenylethylene). The same compound is obtained by the distillation of benzyl sulphide, $(C_6H_5CH_2)_2S$. It crystallizes in thin, colorless leaflets fusing at 120°.

Benzoic Acid, *Phenylformic Acid,* $C_6H_5{-}COOH$, or $C_7H_6O_2$. Benzoic acid is the first aromatic carboxylic acid that we have met. We have seen that the phenols* exhibit acid properties when containing nitro-groups, but we shall meet with a large number of true carboxylic acids among the aromatic compounds. These acids behave in the same manner as the acids of the fatty series.

The hydrogen of the carboxyl is easily replaceable by metals. An aromatic acid, therefore, which contains *one* carboxyl-group as a side-chain is *monobasic.* When *two* carboxyls are present, it is *dibasic,* etc.

The hydroxyl of the carboxyl of the aromatic carboxylic acids can be replaced by chlorine, bromine, or iodine (acichlorides) by ammonia (amides) and by acid rests (anhydrides). By distillation with a formate, they can be converted into their aldehydes, and with the salt of another organic acid, into the corresponding ketones. As they are aromatic acids, chlorine, bromine, iodine, the nitro-group, and the amido-group can be easily introduced into the benzene nucleus, yielding an immense number of derivatives, many of which are, of course, isomeric.

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* The H of the $\equiv C{-}OH$ group, in a tertiary alcohol resembles somewhat the H of the carboxyl group, $O{=}C{-}OH$, in being replaceable by metals. The phenols are tertiary alcohols.

Benzoic acid occurs in gum-benzoin and other gums. It is formed by the oxidation of toluene and benzaldehyde, and also by the simultaneous action of carbonic acid and sodium on brombenzene :

$$C_6H_5Br + Na_2 + CO_2 = C_6H_5{}^{-}COONa + NaBr.$$

It is usually made by heating gum-benzoin, which sublimes the benzoic acid, or by the decomposition of hippuric acid (see later), which occurs in the urine of herbivora, by boiling with chlorhydric acid, which decomposes the hippuric acid into glycocoll and benzoic acid, or finally by heating phenylchloroform, $C_6H_5{}^{-}CCl_3$, with water.

Benzoic acid forms thin, colorless, glittering leaflets with a weak aromatic odor, which fuse at 120° and boil at 249°, although it sublimes under 100°. It is difficultly soluble in cold water, more easily in hot, and very soluble in alcohol and ether.

It is a monobasic acid, and forms salts with bases, which are mostly easily soluble in water. If a benzoate is submitted to dry distillation with an excess of alkali, benzene and a carbonate are formed. This reaction is analogous to the formation of methane from acetic acid (p. 15) :

$$\underset{\text{Sodium acetate}}{CH_3{}^{-}COONa} + NaHO = \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

$$\underset{\text{Sodium benzoate}}{C_6H_5{}^{-}COONa} + NaHO = \underset{\text{Benzene}}{C_6H_6} + Na_2CO_3.$$

If, however, a benzoate is submitted to dry distillation by itself, a ketone, *benzophenone*, $C_6H_5{}^{-}CO{}^{-}C_6H_5$, is produced, in the same manner that acetone is obtained from an acetate :

$$\begin{matrix} CH_3COONa \\ CH_3COONa \end{matrix} = \underset{\text{Acetone}}{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CO} + Na_2CO_3.$$

$$\begin{matrix} C_6H_5{}^{-}COONa \\ C_6H_5{}^{-}COONa \end{matrix} = \underset{\text{Benzophenone}}{\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!CO} + Na_2CO_3.$$

The aromatic ketones are also formed when an acid and a hydrocarbon, both of which belong to the aromatic series, are heated with phosphoric anhydride, which acts as a dehydrating agent:

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + \underset{\text{Benzene}}{C_6H_6} = \underset{\text{Benzophenone}}{C_6H_5{-}CO{-}C_6H_5} + H_2O.$$

Benzophenone, $C_{13}H_{10}O$, crystallizes in prisms fusing at 49° and boiling at 295°. Fuming nitric acid converts it into *dinitrobenzophenone;* nascent hydrogen into *benzhydrol:*

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!CH(OH),$$

(as acetone is converted into isopropyl alcohol). Benzhydrol is a secondary alcohol containing two benzene rests together with the group CH(OH) (just as isopropyl alcohol contains two methyl groups).

By the dry distillation of a mixture of a benzoate and a salt of another organic acid, mixed ketones are obtained, *e. g.*, from an acetate and a benzoate we get *methylphenylketone,* or *acetophenone,* $\begin{matrix} CH_3 \\ C_6H_5 \end{matrix}\!\!>\!CO$, etc.

Sodium amalgam converts this compound into the secondary alcohol, $C_6H_5{-}CH(OH){-}CH_3$.

By treating benzoic acid with phosphorus pentachloride, we obtain

Benzoyl Chloride, C_6H_5COCl, which corresponds to acetyl chloride $CH_3{-}COCl$ (p. 93).

$$C_6H_5COOH + PCl_5 = C_6H_5COCl + HCl + POCl_3.$$

It is a colorless liquid with a pungent odor which causes violent weeping. It boils at 199°. It decomposes gradually with water into benzoic and chlorhydric acids:

$$C_6H_5COCl + H_2O = C_6H_5COOH + HCl.$$

The chlorine of benzoyl chloride is easily replaced by other atoms, or groups. With potassium bromide it yields *benzoyl bromide*, $C_6H_5{-}COBr$; with potassium iodide, *benzoyl iodide*, $C_6H_5{-}COI$; with potassium cyanide, *benzoyl cyanide*, $C_6H_5{-}COCN$; with phosphorus pentachloride at a high temperature (200°), its oxygen is replaced by two chlorine atoms, forming *benzotrichloride:*

$$C_6H_5{-}COCl + PCl_5 = C_6H_5{-}CCl_3 + POCl_3.$$

Benzoyl chloride forms with sodium benzoate *Benzoic Anhydride*, $\begin{matrix} C_6H_5{-}CO \\ C_6H_5{-}CO \end{matrix}\!\!>\!O$:

$$C_6H_5COCl + C_6H_5{-}COONa = NaCl + \begin{matrix} C_6H_5{-}CO \\ C_6H_5{-}CO \end{matrix}\!\!>\!O.$$

Benzoic anhydride forms colorless, prismatic crystals, fusing at 42° and boiling at 350°, insoluble in water, and easily soluble in alcohol and ether.

If, instead of sodium benzoate, benzoyl chloride is mixed with the sodium salt of another acid, mixed anhydrides are obtained. Sodium acetate for instance, gives

Benzoylacetic Anhydride, $\begin{matrix} C_6H_5{-}CO \\ CH_3{-}CO \end{matrix}\!\!>\!O$:

$$C_6H_5{-}COCl + CH_3{-}COONa = NaCl + \begin{matrix} C_6H_5{-}CO \\ CH_3{-}CO \end{matrix}\!\!>\!O.$$

Benzoyl reacts with ammonia, forming *Benzamide:*

$$C_6H_5{-}COCl + NH_3 = C_6H_5{-}CONH_2 + HCl.$$

Benzamide crystallizes in leaflets, fusing at 125° and boiling at 288°. It is soluble in hot water, easily in alcohol and ether. It possesses weak basic properties.

The hydrogen of the carboxyl of benzoic acid can also be substitued by hydrocarbon rests, forming esters, *e.g.*, *methyl benzoic ester*, $C_6H_5{-}COOCH_3$, *ethyl benzoic ester*, $C_6H_6{-}COOC_2H_5$, etc.

These esters are made by dissolving benzoic acid in the

proper alcohol, and leading chlorhydric acid gas through the solution.

The esters can also be easily made by acting on the alcohols with benzoyl chloride. Benzoyl chloride reacts with water, forming benzoic acid and chlorhydric acid:

$$C_6H_5{}^-COCl + HOH = C_6H_5{}^-COOH + HCl.$$

If instead of water, an alcohol (substituted water) is taken, an ester and chlorhydric acid are produced:

$$C_6H_5{}^-COCl + CH_3OH = C_6H_5{}^-COOH_3 + HCl.$$

In this manner *phenyl benzoic ester*, $C_6H_5{}^-COOC_6H_5$, is obtained. It crystallizes in colorless prisms, which fuse at 66°, and are volatile without decomposition.

The derivatives which we have thus far considered have been produced by substitutions in the carboxyl. We shall now take up those in which the substitution takes place in the benzene nucleus.

Monochlorbenzoic acid, $C_6H_4Cl^-COOH$. There are three compounds of this composition, which bear different names.

1) *Chlorsalylic Acid*, $C_6H_4\begin{cases}1\,Cl\\2\,COOH\end{cases}$, is produced by the action of phosphorus chloride on sodium salicylate (see later). It forms colorless crystals fusing at 137°, which are converted into benzoic acid by the action of nascent hydrogen, and into salicylous acid by fusing potassium hydroxide.

$$\underset{\text{Chlorsalylic acid}}{C_6H_4Cl^-CO_2H} + KHO = \underset{\text{Salylic acid}}{C_6H_4(OH)CO_2H} + KCl.$$

2) *Chlorbenzoic Acid*, $C_6H_4\begin{cases}1\,Cl\\3\,COOH\end{cases}$, is obtained directly from benzoic acid by the action of chlorine. Colorless needles fusing at 152°.

3) *Chlordracylic Acid*, $C_6H_4\begin{cases}1\,Cl\\4\,COOH\end{cases}$, is produced by the oxidation of monochlortoluene (1 . 4). Colorless scales fusing at 237°.

The three brombenzoic acids, the three iodobenzoic acids, and the three nitrobenzoic acids are also known.

Nitrobenzoic Acid, $C_6H_4(NO_2)^-COOH$, is formed by the action of fuming nitric acid on benzoic acid. The metanitrobenzoic acid is the chief product, the other two being obtained in lesser amounts. The metanitrobenzoic acid forms needles fusing at 141°. The ortho-compound is also formed by oxidation of orthonitrotoluene. It forms prisms fusing at 147°. The para-compound, which is also obtained by the oxidation of nitrotoluene, forms leaflets fusing at 238°.

They are changed by reduction into amido-acids, which under the proper conditions yield azoxy-, azo-, and hydrazo-compounds.

The nitrobenzoic acids yield, when boiled with alcoholic potassa, *Azoxybenzoic Acids*, $\begin{matrix} C_6H_4(CO_2H)^-N \\ C_6H_4(CO_2H)^-N \end{matrix}\!\!>\!O$.

Sodium amalgam, converts the nitrobenzoic acids into *azobenzoic acids*, $\begin{matrix} C_6H_4(COOH)^-N \\ \| \\ C_6H_4(COOH)^-N \end{matrix}$, which by further reduction pass into *hydrazobenzoic acids*, $\begin{matrix} C_6H_4\,COOH)^-NH \\ | \\ C_6H_4(COOH)^-NH \end{matrix}$, which by the action of silver oxide are converted back into the azo-compounds.

There are also four *dinitrobenzoic acids*, $C_6H_3(NO_2)_2COOH$, and one *trinitrobenzoic acid*, $C_6H_2(NO_2)_3COOH$, known.

Amidobenzoic Acids, $C_6H_4(NH_2)COOH$. The amidobenzoic acids correspond to the nitrobenzoic acids. All three of the monamidobenzoic acids are known. They possess basic properties and unite with acids to form salts, but since they contain the carboxyl group, the hydrogen of which can easily be substituted by metals, they also possess acid properties. This compound may be compared to glycocoll (p. 98).

$CH_2(NH_2)^-COOH$ Glycocoll,
$C_6H_4(NH_2)^-COOH$ Amidobenzoic acid.

The aromatic compounds, however, exhibit some characteristic differences.

The three amidobenzoic acids have also different names :

Anthranilic Acid, $C_6H_4\begin{cases}1\ NH_2\\2\ COOH\end{cases}$, is formed by heating indigo-blue with potassium hydroxide and manganese di-oxide. It crystallizes in glittering yellow leaflets, difficultly soluble in cold water, and easily in

hot. It fuses at 144°, and sublimes without decomposition. It unites with both bases and acids, forming finely crystallizable compounds. On rapid heating, it breaks into aniline and carbonic acid:

$$C_6H_5(NH_2)COOH = C_6H_5{-}NH_2 + CO_2.$$

Amidobenzoic Acid, $C_6H_4\begin{cases}1\ NH_2\\3\ COOH\end{cases}$, is obtained from the corresponding nitrobenzoic acid by reduction with ammonium sulphydrate. Colorless prisms fusing at 173°, subliming without decomposition, difficultly soluble in cold water, easily in hot. It forms salts with both acids and bases. Its ethyl ester, $C_6H_4(NH_2)COOC_2H_5$, and amide, $C_6H_4(NH_2)CO(NH_2)$, are worthy of notice.

Amidodracylic Acid, $C_6H_4\begin{cases}1\ NH_2\\4\ COOH\end{cases}$, is produced by the reduction of nitrodracylic acid with ammonium sulphydrate. It forms colorless rhombohedrons fusing at 186°, and otherwise resembles amidobenzoic acid.

Nitrous acid converts the amidobenzoic acids into diazo-compounds. The diazo-compounds of amidobenzoic acid have been the more thoroughly examined.

If nitrous acid is passed into an alcoholic solution of amidobenzoic acid, small orange crystals separate, which are the amidobenzoic compound of diazobenzoic acid:

$$2\ C_6H_4(CO_2H)NH_2 + HNO_2 = C_6H_4(CO_2H){-}N{=}N{-}NH(CO_2H)C_6H_4 + 2H_2O.$$

If nitrous acid is conducted through an aqueous solution of amidobenzoic acid, however, diazobenzoic acid nitrate is obtained:

$$C_6H_4(CO_2H)NH_2\ .\ HNO_3 + HNO_2 = C_6H_4(CO_2H){-}N{=}N{-}NO_3 + 2\ H_2O.$$

The nitric acid rest, NO_3, of diazobenzoic acid nitrate can be replaced by Cl, HSO_4, etc., in which case the chloride, sulphate, etc., of diazobenzoic acid are formed. On boiling with water, the diazobenzoic acid compound is decomposed, and at the same time, also, the diazobenzene, the double atom of nitrogen being eliminated and hydroxyl taking its place:

$$C_6H_4(CO_2H){-}N{=}N{-}NO_3 + H_2O = C_6H_4(CO_2H)OH + N_2 + HNO_3.$$

An hydroxybenzoic acid is thus obtained.

Of the higher amidated benzoic acids, we shall mention only the diamidobenzoic acid, $C_6H_3(NH_2)_2COOH$, which is obtained by the reduc-

tion of dinitrobenzoic acid, $C_6H_3(NO_2)_2COOH$. It is difficultly crystallizable, owing to its remarkable solubility. As the amido-groups predominate, it does not possess acid properties, *i.e.* does not unite with bases, but forms salts with two molecules of acid.

Since an H of benzene can be replaced by the group SO_3H, forming benzenesulphonic acid, $C_6H_5{-}SO_3H$, an H of the benzene nucleus of benzoic acid can also be substituted by SO_3H, yielding *sulphobenzoic acid.*

Benzoic acid and sulphuric anhydride yield *sulphobenzoic acid*, $C_6H_4\begin{cases}SO_3H\\CO_2H\end{cases}$, a deliquescent, easily decomposable compound, which is dibasic, and forms two series of salts, of which the beautifully crystallizable acid barium salt is worthy of mention. Sulphobenzoic acid can be nitrated. One or both of the hydroxyls can be replaced by Cl, forming $C_6H_4\begin{cases}SO_2OH\\COCl\end{cases}$, *sulphobenzoyl chloride*, and $C_6H_4\begin{cases}SO_2Cl\\COCl\end{cases}$, *sulphobenzoyl dichloride*. With ammonia, these compounds exchange their Cl for NH, yielding $C_6H_4\begin{cases}SO_2OH\\CONH_2\end{cases}$, *sulphobenzamic acid*, and $C_6H_4\begin{cases}SO_2(NH_2),\\CO(NH_2)\end{cases}$ *sulphobenzamide.*

Benzoic acid and benzaldehyde have been shown to be derivatives of benzyl alcohol, which is a true alcohol, and has also the characteristic properties of an alcohol of the fatty series. We shall take up next the consideration of some of its derivatives. As we have already seen (p. 233), benzyl chloride is formed by leading gaseous chlorhydric acid through benzyl alcohol, in the same manner that ethyl chloride is formed from ethyl alcohol :

$$C_6H_5CH_2OH + HCl = C_2H_5CH_2Cl + H_2O.$$

As benzyl chloride behaves as a fatty compound, its chlorine is easily replaceable.

On boiling benzyl chloride with water, benzyl alcohol is regenerated :

$$C_6H_5CH_2Cl + HOH = C_6H_5CH_2OH + HCl.$$

By digestion with alcoholic ammonia, benzyl chloride is converted into the hydrochlorides of *benzylamine:*

$$C_6H_5{}^-CH_2NH_2,$$

dibenzylamine, $(C_6H_5{}^-NH_2)_2NH$, and *tribenzylamine:*

$$(C_6H_5{}^-CH_2)_3N.$$

Benzylamine, $C_6H_5{}^-CH_2{}^-NH_2$, is a liquid boiling at 133°, miscible with water, and possessing strong basic properties.

Dibenzylamine, $(C_6H_5{}^-NH_2)_2NH$, is a liquid insoluble in water. *Tribenzylamine,* $(C_6H_5{}^-CH_2)_3N$, is a crystalline body fusing at 91°, and insoluble in water.

With phosphuretted hydrogen (phosphine) benzyl chloride forms the corresponding phosphines, *benzylphosphine,* $C_6H_5{}^-CH_2{}^-PH_2$, *dibenzylphosphine,* $(C_6H_5{}^-CH_2)_2PH$, and *tribenzylphosphine,* $(C_6H_5{}^-CH_2)_3P$.

Chlorbenzyl forms with potassium cyanide, *benzyl cyanide,* $C_6H_5{}^-CH_2CN$, which on boiling with potassa yields an acid homologous with benzoic acid, $C_6H_5{}^-CH_2{}^-COOH$, *alphatoluic acid,* or *phenylacetic acid:*

$$C_6H_5CH_2CN + 2\,H_2O = C_6H_5CH_2COOH + NH_3.$$

By boiling chlorbenzyl with potassium sulphydrate, the sulphur compound corresponding to benzyl alcohol is produced. It is the mercaptan of the benzyl series, and is called *benzylsulphydrate:*

$$C_6H_5CH_2Cl + KHS = C_6H_5CH_2SH + KCl.$$

It is a colorless liquid with an offensive odor. Its properties resemble those of ethylmercaptan. The *benzyl sulphide,* $(C_6H_5{}^-CH_2)_2S$, and *benzyl disulphide,* $(C_6H_5{}^-CH_2)_2S_2$, have also been produced.

There is a body derived from benzoic acid, which occurs in the animal organism and is called *benzoylglycocoll,* or *hippuric acid,* $C_9H_9NO_3$:

$$\text{Glycocoll} = C_2H_5NO_2 = \frac{CH_2{}^-COOH}{NH_2}$$

$$\text{Hippuric acid} = C_9H_9NO_3 = \frac{CH_2{}^-COOH}{NH^-CO^-C_6H_5}.$$

Hippuric acid occurs as calcium and sodium salts in the urine of the herbivora, and owes its origin to benzoic acid; for, after eating substances containing benzoic acid, hippuric acid is always found in the urine. In fact, the whole amount of benzoic acid taken into the system is thrown off in the urine as hippuric acid. It crystallizes in thick needles, which fuse on heating and decompose by further heating. It is difficultly soluble in water, and forms soluble salts. It is monobasic. On boiling with acids, or alkalis, it breaks into glycocoll and benzoic acid, taking up the elements of water:

$$\frac{CH_2{}^-COOH}{NH^-CO^-C_6H_5} + H_2O = CH_2(NH_2)COOH + C_6H_5COOH.$$

It can be made artificially by the action of benzoyl chloride on silver-glycocoll:

$$C_6H_5COCl + \frac{CH_2{}^-COOH}{NHAg} = \frac{CH_2{}^-COOH}{NH^-COC_6H_5} + AgCl.$$

The di-valent rest, NH, is replaced by O by the action of nitrous acid, forming

Benzoylglycollic acid, $\frac{CH_2{}^-COOH}{O^-CO^-C_6H_5}$, or $C_9H_8O_4$, which is glycollic acid in which the alcoholic hydrogen is replaced by benzoyl.

Ethyl hippuric ester, $\frac{CH_2{}^-COOC_2H_5}{NH^-CO^-C_6H_5}$, and its derivative, *hippuramide*, $\frac{CH_2{}^-CONH_2}{NH^-CO^-C_6H_5}$, are also easily produced.

We shall pass over a large number of the benzyl derivatives, as they are produced in an exactly analogous manner to their corresponding derivatives in the ethyl series.

There are nine dihydroxyl derivatives of toluene possible according to the theory, six having the constitution :

$$C_6H_3(CH_3)(OH)_2,$$

and three the constitution, $C_6H_4(OH)CH_2(OH)$. The first six correspond to the dihydroxyl derivatives of benzene, and resemble quinol, catechol, etc., while the latter three possess both alcoholic and phenol characteristics.

Only a few of these possible compounds are known. *Orcinol,* or *orcin,* $C_7H_8O_2$, belongs to the first six. Orcinol :

$$C_6H_3\begin{cases}OH\\OH\\CH_3\end{cases},$$

is a decomposition-product of many coloring matters derived from lichens (*rocella* and *lecanor*). It is also formed by heating potassium monochlortoluene-sulphonate with potassium hydroxide :

$$C_6H_3\begin{cases}Cl\\SO_3K\\CH_3\end{cases} + 2\,KOH = C_6H_3\begin{cases}OH\\OH\\CH_3\end{cases} + KCl + K_2SO_3.$$

It crystallizes in prisms fusing at 86° and boiling at 290°. Ferric chloride colors it dark violet. On exposure to the air, it takes on a red color owing to partial oxidation. If ammonia is also present, a red coloring matter called orceïn is formed, which is a weak acid and dissolves in alkalis with a purple color, and is precipitated again as a red powder by acids.

Orceïn is the principal constituent of the coloring matter known as *archil.*

If sodium carbonate is added to an ammoniacal solution of orceïn, and the mixture exposed to the air, a bluish-violet liquid is obtained, from which acids precipitate a red powder called *litmus.*

A methyl ether of orcinol is known, $C_6H_3\left\{\begin{matrix}OH\\OCH_3\\CH_3\end{matrix}\right.$, or $C_8H_{10}O_2$, *beta-orcinol.* It is also a product of the decomposition of many lichen coloring matters.

We know also another ether of a dihydroxyl-toluene, viz., *cresol,* $C_6H_3\left\{\begin{matrix}OH\\OCH_3\\CH_3\end{matrix}\right.$, or $C_8H_{10}O_2$.

Cresol occurs in beech-wood tar, together with the monomethyl ether of catechol, *guaiacol,* $C_6H_4\left\{\begin{matrix}OCH_3\\OH\end{matrix}\right.$. Both beta-orcinol and cresol are oils which give precipitates with most of the metallic solutions.

They yield, when treated with potassium chlorate and chlorhydric acid, compounds homologous with chloranil, as:

$$C_7H_2Cl_4O_2 \text{ and } C_8H_4Cl_4O_2.$$

There are two compounds met with in commerce under the name of *creasote* which are essentially different:

1) Coal-tar creasote, which consists principally of phenol with small amounts of cresol, guaiacol, catechol, and phlorol. The so-called crystallized cresote is phenol.

2) Beech-tar creasote, consisting chiefly of cresol and guaiacol.

Chlorinated quinones and quinones of toluene can be produced in the same manner as the chlorinated quinones of benzene. *Trichlortoluenequinone,* $C_6Cl_3\left\{\begin{matrix}O_2\\CH_3\end{matrix}\right.$, and *trichlortoluquinol,* $C_6Cl_3(CH_3)\left\{\begin{matrix}OH\\OH\end{matrix}\right.$, and their derivatives have been obtained.

Only one member of the second class of dihydroxyl-derivatives of toluene, which are partly phenols and partly alcohols, has been obtained, viz., *salicyl alcohol,* or *saligenin,* $C_6H_4\left\{\begin{matrix}1\ OH\\2\ CH_2OH\end{matrix}\right.$, the aldehyde, $C_6H_4\left\{\begin{matrix}OH\\CHO\end{matrix}\right.$, and the acid,

$C_6H_4\begin{cases}OH\\COOH\end{cases}$, derived from it are also known.

The methyl ether of an isomeric salicyl alcohol is also known, viz., *anisyl alcohol*, $C_6H_4\begin{cases}1\ OCH_3\\4\ CH_2OH\end{cases}$, as well as the corresponding aldehyde, $C_6H_4\begin{cases}OCH_3\\CHO\end{cases}^3$, and acid,

$$C_6H_4\begin{cases}OCH_3\\COOH\end{cases}.$$

The three acids corresponding to the three alcohols are all known. They are *salicylic acid*, $C_6H_4\begin{cases}1\ OH\\2\ CO_2H\end{cases}$, *hydroxybenzoic acid*, $C_6H_4\begin{cases}1\ OH\\3\ CO_2H\end{cases}$, and *parahydroxybenzoic acid*,

$$C_6H_4\begin{cases}1\ OH\\4\ CO_2H\end{cases}.$$

Salicylous Alcohol, or *Saligenin*, $C_7H_8O_2$, is produced by the action of a ferment on salicin:

$$\underset{\text{Salicin}}{C_{13}H_{18}O_7} + H_2O = \underset{\text{Sugar}}{C_6H_{12}O_6} + \underset{\text{Saligenin}}{C_7H_8O_2}.$$

Saligenin crystallizes in mother-of-pearl tablets, fusing at 82°. It is difficultly soluble in water, is colored blue by ferric chloride, and by oxidation is converted into salicylous aldehyde and salicylous acid. Dilute acids change it into a resin, *saliretin*, $C_{14}H_{14}O_3$.

Salicylic Aldehyde, or *Salicylous Acid*:

$$C_7H_6O_2,\ C_6H_4(OH)CHO,$$

occurs in the *Spirea ulmaria*. It is formed from salicin by the action of oxidizing agents, and, together with parahydroxybenzoic acid, by the action of chloroform on an alkaline solution of phenol:

$$CHCl_3 + C_6H_5(OH) + NaHO$$
$$= C_6H_4(ONa)CHO + 3\,NaCl + 3\,H_2O.$$

By the action of sodium hydroxide on chloroform, formic acid is formed:

$$CHCl_3 + 3\,NaHO = CHOOH + H_2O,$$

Which in the nascent state unites with phenol, water being eliminated:

$$C_6H_5(OH) + CHOOH = C_6H_4(OH)^-CHO + H_2O.$$

This reaction corresponds exactly to the action of carbonic acid on sodium phenoxide (see under salicylic acid), except that in the one case the aldehyde, in the other the acid, is formed.

It is a liquid with the odor of bitter almonds, boiling at 196°. It is slightly soluble in water, easily in alcohol. It possesses weak acid properties, and, since it is an aldehyde, unites with acid sulphites. Ferric chloride colors it violet-red. Chlorine, bromine, and nitric acid convert it into substitution-products. Salicylous acid is isomeric with benzoic acid.

Salicylic Acid, $C_7H_6O_3$, $C_6H_4(OH)COOH$. The methyl ester of salicylic acid forms the chief constituent of wintergreen oil (*Gaultheria procumbens*). Salicylic acid is formed by fusing salicin, or curmarin, with potassium hydroxide. It crystallizes in prisms fusing at 156°, and is difficultly soluble in cold water, easily in hot. It is properly a monobasic acid, but as it is also a phenol it unites with two molecules of strong bases, such as the alkalis and alkaline earths. Ferric chloride produces a violet color with its salts. On distillation with lime, it breaks into phenol and carbonic acid:

$$C_6H_4(OH)CO_2H = C_6H_5(OH) + CO_2.$$

It can be produced synthetically by adding small pieces of sodium to hot phenol and passing carbonic acid through the mixture. In this way, *sodium salicylate* is obtained:

$$C_6H_5OH + 2\,Na + CO_2 = C_6H_4(ONa)CO_2Na + 2\,H.$$

Sodium salicylate is also formed when sodium phenox-

ide, which is formed from phenol and sodium hydroxide, is heated to 180°, and exposed to a stream of carbonic acid. In this reaction, half of the phenol is regenerated :

$$2\,C_6H_5ONa + CO_2 = C_6H_4(ONa)CO_2Na + C_6H_5OH.$$

This method is used to produce salicylic acid commercially. Salicylic acid has no odor. Its taste is powerfully astringent. It has marked antiseptic properties, and is largely used in the arts as an antiseptic for preserving fruits, wines, etc., and in medicine also as an antiseptic, and in the treatment of many diseases (diphtheria, rheumatism, etc.).

It yields substitution products with chlorine, bromide, iodine, and nitric acid. Its anhydride, $C_6H_4\begin{cases}O\\CO\end{cases}\!\!>$, has also been produced.

Nitrosalicylic Acid, $C_6H_3(NO_2)OH\,.\,COOH$, which is obtained by acting on salicin with nitric acid, yields on reduction *amidosalicylic acid*, $C_6H_3(NH_2)OH\,.\,COOH$. It possesses acid properties.

By the action of ammonia on wintergreen-oil, *salicylamide*, $C_6H_4(OH)CO(NH_2)$, is obtained:

$$C_6H_4\begin{cases}OH\\COOCH_3\end{cases} + NH_3 = C_6H_4\begin{cases}OH\\CONH_2\end{cases} + CH_4O.$$

Salicylamide crystallizes in leaflets fusing at 132°, and boiling at 290° with decomposition, a molecule of water being eliminated, forming salicylimide :

$$C_6H_4\begin{cases}OH\\CONH_2\end{cases} = C_6H_4\!<\!\begin{matrix}NH\\|\\CO\end{matrix} + H_2O,$$

Which is insoluble in water, alcohol, and ether.

Hydroxbenzoic Acid, Oxybenzoic Acid, $C_6H_4\begin{cases}1\ OH\\3\ CO_2H\end{cases}$, or $C_7H_6O_3$.

As we have already seen, nitrous acid converts amidobenzoic acid into diazobenzoic acid nitrate, which decomposes with water into hydroxybenzoic acid. Metahydroxybenzoic acid is also formed by fusing metasulphobenzoic acid with potassium hydroxide.

Hydroxybenzoic acid forms small, colorless, indistinct crystals fusing at 200°, and slightly soluble in water. It is a

monobasic acid, and yields easily substitution products. Its salts are not colored by ferric chloride.

Parahydroxybenzaldehyde, Paroxybenzaldehyde, $C_6H_4 \begin{cases} 1\ OH \\ 4\ CHO \end{cases}$, is formed, besides salicylaldehyde, by the action of chloroform on phenol. It is separated from the latter by distilling the acidified liquid with water, the salicylic aldehyde distilling over with the steam, while the parahydroxybenzaldehyde remains behind, and on cooling crystallizes from the liquid. It forms needles fusing at 115–116°. It is difficultly soluble in water, and its aqueous solution is colored a dirty violet by ferric chloride.

Parahydroxybenzoic Acid, Paroxybenzoic Acid,

$$C_6H_4 \begin{cases} 1\ OH \\ 4\ CO_2H \end{cases}, \text{ or } C_7H_6O_3,$$

Is formed in the same manner from amidodracylic acid, as hydroxybenzoic acid from amidobenzoic acid. It is also obtained by passing carbonic acid over potassium phenoxide. Heated to 200°–210°, in the same manner as salicylic acid, it crystallizes in colorless prisms fusing at 210°. Its reactions are analogous to those of its isomeric acids.

Anisyl Alcohol, $C_6H_4 \begin{cases} 1\ OCH_3 \\ 4\ CH_2OH \end{cases}$, is the methyl ether of the alcohol derived from parahydroxybenzoic acid. It is made from anisyl aldehyde, and forms colorless needles fusing at 25° and boiling at 258°.

Anisyl Aldehyde, $C_6H_4 \begin{cases} OCH_3 \\ CHO \end{cases}$, is obtained from anise-oil or fennel-oil by heating with dilute nitric acid. It is a colorless liquid boiling at 248°, with a spicy odor. It forms crystalline compounds with acid alkali sulphites, and is oxidized by the oxygen of the air into anisic acid.

Anisic Acid, $C_6H_4 \begin{cases} OCH_3 \\ CO_2H \end{cases}$, is made from anise-oil, or directly from anisyl aldehyde. It is also obtained artifically by

methylating parahydroxybenzoic acid. Colorless needles fusing at 185°. It is a monobasic acid.

The carboxyl derivatives are the only other hydroxyl derivatives of toluene which are known.

1) The principal representatives of the six theoretically possible acids, $C_6H_3\begin{cases}(OH)_2\\CO_2H\end{cases}$, are *hydroxysalicylic acid* (1 . 2 . 5), *parahydroxysalicylic acid, and protocatechuic acid* (1 . 3 . 4).

Hydroxysalicylic and parahydroxysalicylic acids are formed from the corresponding amides of salicylic acid, by conversion into the diazo-compounds, and then into the hydroxyl-compounds. Protocatechuic acid is a decomposition-product of many tannic acids (catechin, etc.). It crystallizes in colorless needles containing a molecule of water, which fuse at 199° and then break into carbonic acid and catechol.

The dimethyl ether of protocatechuic acid, $C_6H_3\begin{cases}(OCH_3)_2\\COOH\end{cases}$, is known as *veratric acid*, and exists in sabadilla-seeds. It forms needles fusing at 180°.

The methyl ether of the aldehyde of protocatechuic acid, $C_6H_3\begin{cases}OCH_3\\OH\\CHO\end{cases}$, is intimately related to protocatechuic acid. It occurs in the vanilla bean and is called *vanillin*. Vanillin is formed by the oxidation of a substance, $C_{10}H_{12}O_3$, obtained from coniferin (see later). It crystallizes in needles, fusing at 80°, and possesses an intense odor of vanilla.

The decomposition-product, $C_{10}H_{12}O_3$, which is obtained directly from coniferin, has probably the constitution, $C_6H_3\begin{cases}OCH_3\\OH\\CH{=}CH{-}CH_2OH\end{cases}$, and would hence stand in intimate relation to cinnamic alcohol (see later). *Hydroxysalicylic Acid* is formed by the action of fusing potassium hydroxide on a substance, $C_{14}H_{10}O_5$, *gentisin*, which occurs in the gentian root.

These acids are decomposed by distillation as follows:

Hydroxysalicylic acid into carbonic acid and quinol.

Protocatechuic acid into carbonic acid and catechol.

Parahydroxysalicylic acid into carbonic acid and resorcinol.

2) The last hydroxyl derivative of toluene is **Gallic Acid,** $C_6H_2\begin{cases}(OH)_3\\CO_2H\end{cases}$, or $C_7H_6O_5$. Gallic acid is formed from tannic acid, or digallic acid.

It crystallizes, with one molecule of water, in fine glittering needles, which lose their water of crystallization at 100°, and fuse at 200°. It possesses a weak acid and astringent taste. With ferric salts it gives a blackish-blue color, and does not precipitate glue-solutions. It is difficultly soluble in cold water, easily in hot. It is properly a monobasic acid, but all four of its hydroxyl-hydrogen atoms can be replaced by metals. On heating, it is decomposed into carbonic and pyrogallic acids:

$$C_6H_2\begin{cases}(OH)_3\\CO_2H\end{cases} = C_6H_3(OH)_3 + CO_2.$$

The salts of gallic acid absorb oxygen from the air, passing into a higher state of oxidation. They precipitate gold and silver at once from solutions of their salts, and are hence used in photography.

Digallic Acid, **Tannic Acid, Tannin,** $C_{14}H_{10}O_9$, is an ester of gallic acid, $C_6H_2(OH)_3{-}CO{-}O{-}C_6H_2(OH)_2{-}CO_2H$. It exists in nut-galls, sumach, and many other plants. It can be produced from gallic acid by heating with phosphorus oxychloride, or with a solution of arsenic acid. It is usually obtained from nut-galls by extraction with ether containing alcohol.

It forms an amorphous mass easily soluble in water, with an astringent taste. Ferric salts produce in it a deep blue-black precipitate. It is preciptated from its solution by glue solution, tartar emetic, and particularly by animal skin, which is thereby converted into leather (tanning).

The tannic acids which occur in oak-bark, quinine barks, catechu, fern-root, torentill-root, fustic, coffee-beans, etc., are similar, but have not yet been thoroughly examined.

Amido-derivatives of toluene. One amido-derivative of toluene, viz., *benzylamine*, $C_6H_5{}^{-}CH_2(NH_2)$, has already been mentioned. In this compound, the amido-group is in the side-chain. If, however, the amido-group substitutes the hydrogen of the benzene nucleus, an amido-derivative will be obtained which exists in three isomeric modifications. These amido-toluenes are called *toluidines*, and are obtained according to the usual method, by reducing the corresponding nitrotoluenes.

The two liquid nitrotoluenes yield on reduction two liquid toluidines, $C_6H_4\left\{\begin{matrix}1\,NH_2\\2\,CH_3\end{matrix}\right.$, (*pseudotoluidine*) and

$$C_6H_4\left\{\begin{matrix}1\,NH_2\\3\,CH_3\end{matrix}\right.$$

Both of them boil at 198°, give a violet color with chloride of lime solution, and resemble aniline in their general behavior. The third nitrotoluene, which is solid at ordinary temperatures, yields a crystalline toluidine, $C_6H_4\left\{\begin{matrix}1\,NH_2\\4\,CH_3\end{matrix}\right.$, which fuses at 45° and boils at 198°.

All three of these toluidines, like aniline, yield a great number of derivatives. The derivatives form three isomeric series, and differ from the corresponding aniline derivatives by the plus increment of CH_3. We shall not consider them further.

Following toluidine, we shall take up a number of complicated compounds which play an important part as coloring matters in the arts, and which are formed by heating mixtures of aniline and toluidine (high-boiling anilines) with weak oxidizing agents. They are known as the *aniline colors*.

The simplest of these colors, and the one from which the most of the others are derived, is *fuchsine*. It is made by heating the so-called commercial aniline with arsenic acid, nitrobenzene, etc.

Fuchsine is usually the hydrochloride or acetate of the base, $C_{20}H_{19}N_3$, *rosaniline*, which does not exist in the free state, and has the composition, $C_{20}H_{19}N_3 \cdot HCl$. It crystallizes in rhomboic tablets of a superb, glittering green color, is slightly soluble in water, and easily in alcohol, with an intense red color. It dyes silk and wool red. On the addition of chlorhydric acid to a solution of rosaniline, the red color disappears, and by the addition of hot concentrated chlorhydric acid, the *trihydrochloride*, $C_{20}H_{19}N_3 \cdot 3\,HCl$, separates in yellowish-brown needles, which by heating, or with water, are converted into fuchsine.

If ammonia is added to a solution of fuchsine, particularly the acetate, a precipitate is obtained which, when pure, is perfectly colorless. As it is converted back into fuchsine with extreme ease by acids, and even by the carbonic acid of the air, it has been considered as the free base of fuchsine, and is called *rosaniline*. It has the composition:

$$C_{20}H_{21}N_3O = C_{20}H_{19}N_3 + H_2O.$$

Fuchsine is converted by nascent hydrogen (*e.g.*, zinc and chlorhydric acid) into a compound containing two atoms of hydrogen more than fuchsine. This body has the composition, $C_{20}H_{21}N_3$, and is called *leucaniline*. Both the base and its salts are colorless.

Leucaniline, $C_{20}H_{21}N_3$, is derived from a hydrocarbon, $C_{20}H_{16}$, which has the constitution:

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!\rangle CH\text{-}C_6H_4CH_3,$$

Diphenyltolylmethane, of which it is the triamido derivative:

$$\begin{matrix} NH_2\text{-}C_6H_4 \\ NH_2\text{-}C_6H_4 \end{matrix}\!\!\rangle CH\text{-}C_6H_3\langle\!\!\begin{matrix} CH_3 \\ NH_2 \end{matrix}.$$

Rosaniline hydrate, $C_{20}H_{21}N_3O$, however, is the hydroxyl derivative of leucaniline, and has the constitution :

$$(NH_2{-}C_6H_4)_2{=}C(OH){-}C_6H_3\begin{cases}CH_3\\NH_2\end{cases}.$$

The compound, $C_{20}H_{19}N_3$, the salts of which constitute fuchsine, is a peculiar condensation-product of rosaniline, formed by the elimination of water :

$$\begin{matrix}NH_2{-}C_6H_4\\NH_2{-}C_6H_4\end{matrix}\Big\rangle C\Big\langle\begin{matrix}C_6H_3{-}CH_3\\|\\NH\end{matrix}.$$

The salts of leucaniline yield fuchsine again by oxidation.

It is easy to see that compounds similar to fuchsine will be formed when instead of toluidine higher methylated anilines are heated with weak oxidizing agents.

The atoms of hydrogen which are in combination with the nitrogen can easily be replaced by hydrocarbon rests. By heating rosaniline with methyl iodide, or chloride, *methyl violet* is obtained. It can also be produced by heating dimethylaniline with cupric nitrate and salt. It has the composition, $C_{20}H_{14}(CH_3)_5N_3$. HCl. The *ethyl violet* corresponds with it in every way. On heating rosaniline with aniline at 180°, a blue coloring matter, *aniline blue*, is obtained, which is a triphenylrosaniline :

$$C_{20}H_{16}(C_6H_5)_3N_3 \,.\, HCl.$$

Methyl violet in the dry state is golden yellow. Aniline blue is a bluish-brown powder with a coppery luster.

Iodine green has the composition :

$$C_{20}H_{14}(CH_3)_5N_3 . CH_3Cl + H_2O,$$

and crystallizes in prisms with a superb cantharides-green metallic luster. It is formed by heating rosaniline acetate with methyl chloride and methyl alcohol.

Besides fuchsine, there is formed by the action of arsenic acid, etc., on aniline containing toluidine, the salt of another

base, which on account of its yellow color is called *chrysaniline*, $C_{20}H_{17}N_3$.

Crysaniline unites with one and two molecules of acids to form salts.

We have, then :

Chrysaniline,	$C_{20}H_{17}N_3$
Rosaniline,	$C_{20}H_{19}N_3$
Leucaniline,	$C_{20}H_{21}N_3$

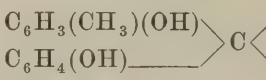
And from rosaniline :

Pentamethylrosaniline,	$C_{20}H_{14}(CH_3)_5N_3$	yielding aniline violets.
Penta-ethylrosaniline,	$C_{20}H_{14}(C_2H_5)_5N_3$	
Triphenylrosaniline,	$C_{20}H_{16}(C_6H_5)_3N_3$	yielding aniline blue.

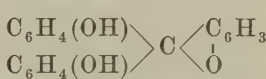
Under the name of *mauve*, a violet dye is met with in the arts, which is the hydrochloride of *mauveïne*, $C_{27}H_{24}N_4$. Mauveïne is formed by the action of strong oxidizing agents, *e.g.*, potassium chromate, on aniline containing toluidine. Its constitution is not known.

If a solution of aniline in chlorhydric acid is treated with cupric chloride and potassium chlorate, a green precipitate is formed which becomes still more highly oxidized by the air, forming a black. It is called *aniline-black*. Its composition is not known.

Rosolic Acid, $C_{20}H_{16}O_3$, stands in intimate relation with rosaniline. Its constitution is either :



or



It is formed by heating phenol with oxalic acid and sulphuric acid at 150°. It forms glittering red prisms with a

blue or green reflex. It fuses with decomposition over 220°. Reducing agents convert it into *leucorosolic acid*, $C_{20}H_{18}O_3$, which crystallizes from glacial acetic acid in thick, colorless prisms.

Leucorosolic acid is the trihydroxyl-derivative of diphenyltolymethane, and rosolic acid is the oxidation product of it.

Xylene.

Only the more important of the benzene derivatives which contain more hydrocarbon rests than one methyl, will be considered. When two H's of benzene are substituted by methyl-groups, three isomeric dimethylbenzenes are obtained:

$$C_6H_4(CH_3)_2, \quad \text{or} \quad C_8H_{10},$$

which are also isomeric with ethylbenzene:

$$C_6H_5{}^-C_2H_5, \quad \text{or} \quad C_8H_{10}.$$

The dimethylbenzenes can be produced artificially. They occur, together with benzene and toluene, in coal-tar, and are called *xylenes*. Ethylbenzene can only be obtained artificially. Dimethylbenzenes are formed from the corresponding chlor- or bromtoluenes by the action of methyl iodide and sodium; ethylbenzene from chlorbenzene, ethyl iodide and sodium. The xylenes boil at about 140°, ethyl benzene at 134°.

They resemble benzene and toluene in their properties. Chlor-, brom-, and iodo-derivatives of them are known.

The phenols of xylene and ethylbenzene are partly known. They possess the characteristic properties of phenols, and are so little different from ordinary phenol, that they may be omitted. For similar reasons the alcohol derived from dimethylbenzene, $C_6H_4\begin{cases}CH_3\\CH_2OH\end{cases}$, *tolyl alcohol*, will not be further considered.

The acids derived from xylene and ethylbenzene, however, possess a greater interest:

$$C_6H_4\begin{cases}CH_3\\CO_2H\end{cases}, \quad C_6H_4\begin{cases}CO_2H\\CO_2H\end{cases} \quad \text{and} \quad C_6H_5{}^-CH_2{}^-CO_2H.$$

If a dimethylbenzene is treated with oxidizing agents, the methyl is oxidized into carboxyl, and there is produced, according to the energy of the oxidation :

$$C_6H_4 \begin{cases} CH_3 \\ COOH, \end{cases} \quad \text{Toluic acid,}$$

$$\text{or} \quad C_6H_4 \begin{cases} COOH \\ COOH, \end{cases} \quad \text{Phthalic acid.}$$

By oxidation of ethylbenzene, however, the carbon atom which is united to the benzene-nucleus is oxidized so that carbonic acid and benzoic acids are obtained :

$$C_6H_5{}^{-}CH_2{}^{-}CH_3 + 3\,O_2 = C_6H_5COOH + CO_2 + 2\,H_2O.$$

There is, however, an acid known which is isomeric with the three toluic acids, and which is a derivative of ethylbenzene, viz., *phenylacetic acid,* or *alphatoluic acid :*

$$C_6H_5{}^{-}CH_2{}^{-}COOH.$$

There are hence three toluic acids and three phthalic acids, and, in addition, the alphatoluic acid. *Orthotoluic acid,* $C_8H_8O_2$, forms long fine needles fusing at 102°, *metatoluic acid,* needles fusing at 109°, and *paratoluic acid,* colorless needles fusing at 178°.

Alphatoluic Acid is obtained by boiling benzyl cyanide with potassa, and forms leaflets resembling benzoic acid, which fuse at 76.5° and boil without decomposition at 261–262°.

By oxidation with potassium chromate and sulphuric acid, the three toluic acids are converted into the three corresponding phthalic acids, while the alphatoluic acid is transformed into benzoic acid.

Phenylglycollic, or *Mandelic Acid,* $C_6H_5{}^{-}CH(OH){}^{-}COOH$, is a derivative of alphatoluic acid, or *phenylacetic acid,* and stands in the same relation to phenylacetic acid as glycollic acid to acetic acid :

$C_6H_5{-}CH_2{-}COOH$	$C_6H_5{-}CH(OH){-}COOH$
Benzoic acid	Phenylglycollic acid
$H{-}CH_2{-}COOH$	$H{-}CH(OH){-}COOH.$
Acetic acid	Glycollic acid

Mandelic acid is formed by boiling a mixture of benzaldehyde and cyanhydric acid with chlorhydric acid :

$$C_6H_5{-}CHO + CNH + 2\,H_2O = C_6H_5{-}CH(OH){-}COOH + NH_3,$$

the reaction being analogous to the formation of lactic acid from acetaldehyde. It crystallizes in tablets or prisms fusing at 115°.

It is converted into phenylglyoxylic acid by oxidation with dilute nitric acid. On further oxidation it passes into benzaldehyde and carbonic acid, and finally into benzoic acid. Iodchydric acid reduces it to alphatoluic acid.

Phenylglyoxylic acid, $C_6H_5{-}CO{-}COOH$, can also be obtained by the decomposition of benzoyl cyanide. It forms crystals fusing at 66°.

When the toluic acids are treated with oxidizing agents, the second methyl group is, as we have seen, also oxidized to carboxyl, forming compounds of the formula $C_6H_4\langle^{COOH}_{COOH}$. These dicarboxylic acids of benzene are called *phthalic acids*. They are dibasic, and exist in three isomeric modifications.

1) *Phthalic Acid*, $C_6H_4\{^{1\ COOH}_{2\ COOH}$, or $C_8H_6O_4$. This acid is best obtained by the oxidation with nitric acid of a hydrocarbon, naphthalene, $C_{10}H_8$, which we shall meet later on. It crystallizes in glittering leaflets which are quite easily soluble in hot water. It is a dibasic acid. It fuses at 173°, decomposing into water and *phthalic anhydride*, $C_6H_4\langle^{CO}_{CO}\rangle O$. Numerous chlorine and nitro-substitutions of it are known. Phthalic anhydride forms long, glittering needles fusing at 127° and boiling at 277°.

2) *Isophthalic Acid,* $C_6H_4\begin{cases}1\ COOH\\3\ COOH\end{cases}$, is usually made by the oxidation of the xylene contained in coal-tar. It crystallizes in fine needles fusing over 300°, and is difficultly soluble in hot water.

3) *Terephthalic Acid,* $C_6H_4\begin{cases}1\ COOH\\4\ COOH\end{cases}$, is obtained, besides isophthalic acid, by the oxidation of the xylene from coal-tar. It is an amorphous powder which sublimes at a high temperature without fusing.

All three of the phthalic acids yield benzene by distillation with lime :

$$C_6H_4(COOH)_2 = C_6H_6 + 2\,CO_2.$$

Of the numerous other derivatives of the hydrocarbon, C_8H_{10}, we shall only mention the amido-compounds. The mixture of dimethylbenzenes and xylenes, which are contained in coal-tar are converted by the action of nitric acid into nitroxylenes, and these by reduction into amidoxylenes. These amidoxylenes, form a mixture of extremely similar bodies which have not yet been separated, and hence bear the common name of *xylidine.* Xylidine is an oily liquid boiling at 216°, and resembling aniline very much. With reagents, it yields derivatives analogous to those of aniline. Like aniline, xylidine possesses basic properties.

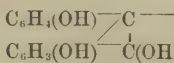
By treating phthalic anhydride with phenol and concentrated sulphuric acid, *phenolphthaleïn* is formed :

$$C_{20}H_{14}O_4 = \begin{matrix}C_6H_4(OH)\\C_6H_4(OH)\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}C_6H_4\\O\text{—}\end{matrix}\!\!>\!CO.$$

It is a yellowish-white powder which is soluble in alkalis with a red color. On boiling its alkaline solution with zinc dust, it takes up two atoms of hydrogen, yielding *phenolphthalin :*

$$C_{20}H_{16}O_4 = \begin{matrix}C_6H_4(OH)\\C_6H_4(OH)\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}C_6H_4\text{-}COOH\\H\end{matrix},$$

which crystallizes in small needles, and is easily oxidized into phenolphthaleïn. It is soluble in concentrated sulphuric acid, with a reddish yellow color. From this solution, water precipitates *phenolphthalidin*, $C_{20}H_{14}O_3$:

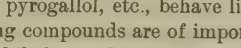


as a yellowish-green precipitate. *Phthalidin* is converted by oxidizing agents into *phenolphthalideïn*, $C_{20}H_{14}O_4$, which is isomeric with the phthaleïn.

The various hydroxyl derivatives of benzene, as catechol, resorcinol, quinol, orcinol, pyrogallol, etc., behave like phenol.

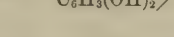
The following compounds are of importance :

Resorcinol-phthaleïn-anhydride, fluoresceïn :



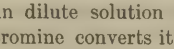
which is formed by heating phthalic anhydride with resorcinol at 200°. It is a yellowish-red powder which is easily soluble in alkalis and alkaline carbonates, and in dilute solution possesses a beautiful yellowish-green fluorescence. Bromine converts it into *tetrabromfluoresceïn, eosin*, $C_{20}H_8Br_4O_5$, which crystallizes from alcohol in flesh-colored crystals. It is quite a strong dibasic acid and yields beautifully crystallizable salts. Its alcoholic solution, on the smallest addition of an alkali, assumes a beautiful yellowish-green fluorescence. The potassium salt, $C_{20}H_6Br_4O_5K_2$, crystallizes with varying amounts of water, and is a valuable dye.

On evaporating fluoresceïn with an excess of sodium hydroxide solution, one molecule of resorcinol splits out, and *mono-resorcinol-phthaleïn*, $C_{14}H_{10}O_5$, is produced. On treating eosin in the same manner, *dibrom-resorcinolphthaleïn :*



is obtained.

On heating pyrogallol with phthalic anhydride at 200°, *galleïn*, $C_{20}H_{14}O_8$:



is formed. It is a brownish-red powder which dissolves in potassium and sodium hydroxide solutions with a blue color, and in ammonia with a

violet color. It loses the elements of water at 180°, and is converted into *gallein anhydride*, $C_{20}H_{12}O_7$. Nascent hydrogen converts it into *gallin*, $C_{20}H_{18}O_7$.

We see from the above, that phthalein is a derivative of triphenylmethane :

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} C_6H_5 \\ H \end{matrix},$$

and stands in intimate relation to rosolic acid, and hence also to rosaniline.

Cumene.

The derivatives of benzene which contain nine carbon atoms are represented by three trimethylbenzenes :

$$C_6H_3(CH_3)_3,$$

three methylethylbenzenes, $C_6H_4(CH_3)(C_2H_5)$, and two propylbenzenes, $C_6H_5{-}C_3H_7$. All of them have the general formula, C_9H_{12}.

A mixture of two trimethylbenzenes occurs in coal-tar. One is pseudocumene, (1 . 3 . 4). The other, which can also be obtained by treating acetone with dehydrating agents, is called *mesitylene :*

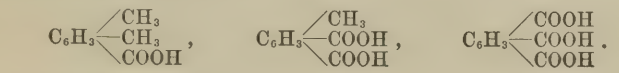
$$3\,CH_3{-}CO{-}CH_3 = C_6H_3(CH_3)_3 + 3\,H_2O.$$

This peculiar condensation of acetone takes place in the following manner. The oxygen of each molecule of acetone unites with two hydrogen atoms of another molecule, forming a double binding between each of the molecules. The trimethylbenzene thus produced contains the methyls in the 1 . 3 . 5 position.

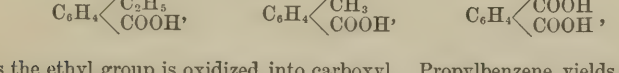
These hydrocarbons are distinguished chiefly by the differences in the properties of their nitro-compounds. Two of the *methylethylbenzenes* are known. They are made by ethylating toluene.

Isopropylbenzene, or *Cumene*, is obtained by distilling cumic acid with lime, and also from brombenzene and propyl bromide.

According to the energy of the oxidation, the trimethylbenzenes yield three oxidation-products :



Methylethylbenzene, however,



as the ethyl group is oxidized into carboxyl. Propylbenzene yields only benzoic acid.

The three trimethylbenzenes boil between 163–165°; *methylethylbenzenes* from 159–162°; propylbenzene at 157°, and cumene at 151°.

The pseudocumene, which occurs in coal-tar, yields the following products on oxidation.

Xylic acid, $C_6H_3\{^{1\,CH_3}_{3\,CH_3}_{4\,COOH}$, or $C_9H_{10}O_2$, which crystallizes in prisms fusing at 126°.

Paraxylic acid, $C_6H_3\{^{1\,COOH}_{3\,CH_3}_{4\,CH_3}$, or $C_9H_{10}O_2$, crystallizing in prisms fusing at 163°.

Xylidic acid, $C_6H_3\{^{1\,COOH}_{3\,CH_3}_{4\,COOH}$, or $C_9H_8O_4$, amorphous and fusing at 282°.

The mesitylene, $C_6H_3\{^{1\,CH_3}_{3\,CH_3}_{5\,CH_3}$, which is obtained from acetone, yields on oxidation with dilute nitric acid :

Mesitylenic acid, $C_6H_3\{^{1\,CH_3}_{3\,CH_3}_{5\,COOH}$, or $C_9H_{10}O_2$, crystallizing in needles fusing at 166°.

Uvitic acid, $C_6H_3\begin{cases}1\ CH_3\\3\ COOH\\5\ COOH\end{cases}$, or $C_9H_8O_4$, needles fusing at 288°.

Trimesic acid, $C_6H_3\begin{cases}1\ COOH\\3\ COOH\\5\ COOH\end{cases}$, or $C_9H_6O_6$, which crystallizes in prisms soluble in water, fuses at above 300° and sublimes without decomposition.

The two other tricarboxylic acids, $C_9H_6O_6$, isomeric with trimesic acid, are also known. They are produced from mellitic acid (see later), and are called *trimellitic acid* (1 . 2 . 4), and *hemimellitic acid* (1 . 2 . 3).

The third trimethylbenzene has not yet been examined.

There remains still to be mentioned an acid which is derived from *paramethylethylbenzene*. It is not directly obtainable from it, but from di-ethylbenzene. It is *ethylbenzoic acid*, and its formula is, $C_6H_4\begin{cases}C_2H_5\\COOH\end{cases}$. It crystallizes in small prisms fusing at 110°.

From isopropylbenzene is derived *hydro-atropic acid:*

$$C_6H_5\text{-}CH\begin{cases}CH_3\\COOH\end{cases},$$

which is formed by the reduction of *atropic acid* (see later). It is a liquid boiling at 265°.

Benzopropionic acid, or *hydrocinnamic acid:*

$$C_6H_5\text{-}CH_2\text{-}CH_2\text{-}COOH,$$

is a derivative of *propylbenzene*, although it cannot be directly produced from it. It is formed by the action of nascent hydrogen on cinnamic acid, and crystallizes in leaflets fusing at 47°. It is easily soluble in hot water, and is converted by oxidation into benzaldehyde and benzoic acid. Both of these acids are isomeric with xylic, paraxylic, mesitylenic, and ethylbenzoic acids.

From propylbenzene there is also a group of compounds derived which occur in nature, and which stand in the same relation to propylbenzene as allyl alcohol to its aldehyde, viz., *cinnyl alcohol, cinnamic aldehyde*, and *cinnamic acid:*

$HCH_2{-}CH_2{-}CH_3$ Propane	$C_6H_5{-}CH_2{-}CH_2{-}CH_3$ Cumene
$HCH{=}CH{-}CH_2(OH)$ Allyl alcohol	$C_6H_5{-}CH{=}CH{-}CH_2(OH)$ Cinnyl alcohol
$HCH{=}CH{-}CHO$ Acrolein	$C_6H_5{-}CH{=}CH{-}CHO$ Cinnamic aldehyde
$HCH{=}CH{-}COOH$ Acrylic acid	$C_6H_5{-}CH{=}CH{-}COOH$ Cinnamic acid

Liquid storax-balsam contains a body which, when purified by boiling the storax with sodium carbonate and crystallizing from a mixture of alcohol and ether, forms odorless and tasteless needles, fusing at 44°. It is called *styracin*, and is the cinnyl ester of cinnamic acid, $C_9H_9O{-}C_9H_7O$. On boiling with potassa, styracin is decomposed into cinnyl alcohol and cinnamic acid:

$$C_9H_9O{-}C_9H_7O + H_2O = C_9H_{10}O + C_9H_8O_2.$$

Cinnyl Alcohol, $C_6H_5{-}CH{=}CH{-}CH_2(OH)$, or $C_9H_{10}O$, is *phenyl-allyl alcohol;* it is obtained by boiling styracin with potassa, and distils over with the steam, forming a colorless oil swimming on water. On standing, this oil solidifies to long, glittering needles, which have an odor of hyacinths. It fuses at 33° and distils unchanged at 250°. Cinnyl alcohol is but slightly soluble in water, easily in alcohol and ether. On heating with boric anhydride, it is converted into *cinnyl ether,* $C_9H_9{-}O{-}C_9H_9$, which is a liquid insoluble in water. When cinnyl alcohol is digested with gaseous chlorhydric acid, *cinnamic chloride, or styrylic chloride,* $C_6H_5{-}CH{=}CH{-}CH_2Cl = C_9H_9Cl$, is formed. It is an oil insoluble in water, and converted by alcoholic ammonia into *cinnamine,* $C_9H_9(NH_2)$.

Cinnyl alcohol is converted by oxidation into cinnamic aldehyde.

Cinnamic Aldehyde, $C_6H_5{-}CH{=}CH{-}CHO$, or C_9H_8O, is formed by the oxidation of cinnyl alcohol, and also by heating

a mixture of benzaldehyde and aldehyde with chlorhydric acid :

$$C_6H_5{}^-CHO + CH_3{}^-CHO = C_6H_5{}^-CH{=}CH{}^-CHO + H_2O.$$

We have already had examples, under ordinary aldehyde, of this condensation of two aldehydes with elimination of water. On digesting ordinary aldehyde with chlorhydric acid, water is eliminated, and two molecules of aldehyde unite, forming crotonic aldehyde (p. 139):

$$CH_3{}^-CHO + CH_3{}^-CHO = CH_3{}^-CH{=}CH{}^-CHO + H_2O.$$

Cinnamaldehyde occurs in nature as the chief constituent of cinnamon-oil, from which it is usually made. It is a colorless liquid, insoluble in water and sinking therein. It has the odor of cinnamon, and, as it is an aldehyde, it unites with acid alkali sulphites, and is oxidized (by the oxygen of the air) to cinnamic acid.

Cinnamic Acid, $C_6H_5{}^-CH{=}CH{}^-COOH$, or $C_9H_8O_2$, is obtained, besides cinnyl alcohol, from styracin. It is present, together with styracin, in liquid storax, and is separated from it by treatment with sodium carbonate. The cinnamic acid drives out the carbonic acid and forms sodium cinnamate, which is soluble in water. Chlorhydric acid precipitates the free cinnamic acid from this solution. It also occurs in old cinnamon-oil, the cinnamic aldehyde having gradually become oxidized into the acid.

It can be made synthetically by heating benzaldehyde with acetic anhydride and dry sodium acetate, in which case the latter acts as a dehydrating agent :

$$2\,C_6H_5{}^-CHO + (CH_3{}^-CO)_2O = 2\,C_6H_5{}^-CH{=}CH{}^-COOH + H_2O.$$

The homologues of cinnamic acid can also be obtained by this method. Benzaldehyde and propionic anhydride give *phenylisocrotonic acid*,

$$C_6H_5{}^-CH{=}CH{}^-CH_2{}^-COOH.$$

Benzaldehyde and butyric anhydride, *phenylangelic acid*, etc.

It forms prismatic crystals fusing at 133° and boiling at

290°. It is difficultly soluble in cold water, easily in hot. With chlorine, bromine, iodine, and nitric acid, it yields substitution-products. Its carboxyl-hydrogen is easily replaced by metals and hydrocarbon rests, forming salts and esters.

Phosphorus pentachloride converts it into *cinnamyl chloride*, C_9H_7OCl, an oil, which with water decomposes into cinnamic acid, with ammonia into *cinnamyl amide*, $C_9H_7ONH_2$. On oxidation, it passes into benzaldehyde and benzoic acid. Nascent hydrogen converts it into *hydrocinnamic*, or *phenyl-propionic acid*, $C_6H_5{-}CH_2{-}CH_2{-}COOH$. Sodium cinnamate and cinnamyl chloride yield *cinnamic anhydride*, $\begin{matrix}C_9H_7O\\C_9H_7O\end{matrix}\!\!>\!O$, a colorless, crystalline mass fusing at 127°, which also forms numerous substitution-products.

When cinnamic acid is heated with lime, it breaks, analogously to benzoic acid, into carbonic acid and a hydrocarbon, *styrolene*, or *phenylethylene*, C_8H_8 :

$$C_9H_8O_2 = C_8H_8 + CO_2.$$

Styrolene, Styrol, or *Cinnamene*, $C_6H_5{-}CH{=}CH_2$, or C_8H_8, occurs in liquid storax, and is a colorless, strongly refractive liquid with an odor resembling that of benzene. It boils at 146° and is insoluble in water. When heated to 200° in closed vessels, it is converted into a solid and odorless mass, which is an isomeric styrolene, known as *metastyrolene*. Its formula is probably $3\,C_8H_8$. At 320°, it is transformed back into ordinary styrolene. When styrolene is heated to 170° with chlorhydric acid, it is converted into an oily liquid, which is probably $2\,C_8H_8$ *distyrolene*. Nitric acid converts styrolene into nitro-compounds. Bromine yields two addition-compounds, $C_8H_8Br_2$, which, on heating with alcoholic potassa, are converted into bromstyrolene, C_8H_7Br, and then into *phenyl-acetylene*, $C_8H_8 = C_6H_5{-}C{\equiv}CH$, an oil which boils at 140°.

There are two esters of cinnamic acid which occur in nature, viz. :

1) *Benzylcinnamic Ester, or Cinnameïn,* $C_9H_7O_2{}^-C_7H_7$. It occurs in balsams of Peru and Tolu. It forms small, glittering prisms with a pleasant odor and a sharp, spicy taste, which fuse at 39°.

2) *Cinnamyl Cinnamic Ester, or Styracin,* $C_9H_7O_2{}^-C_9H_9$, is also contained in liquid storax. It forms small, colorless needles without taste or smell, fusing at 44°.

Cumaric Acid, Hydroxycinnamic Acid,

$$C_9H_8O_3 = C_6H_4\begin{cases}1\ OH\\2\ CH{=}CH{-}COOH\end{cases}$$

stands in intimate relation to cinnamic acid. It is obtained from cumarin (see later) and crystallizes in colorless needles fusing at 195°, and soluble in hot water. On fusion with potassium hydroxide, it yields acetic and salicylic acids:

$$C_6H_4\begin{cases}1\ OH\\2\ CH{=}CH{-}CO_2H\end{cases} + 2\,KHO = C_6H_4\begin{cases}1\ OH\\2\ CO_2K\end{cases} + CH_3{-}CO_2K + H_2.$$

Cumaric Anhydride, or Cumarin, $C_6H_4\begin{cases}O\\CH{=}CH{-}CO\end{cases}$, occurs in many plants (*Asperula odorata*), and especially in the tonka-bean. It is produced synthetically from the sodium compound of salicylic aldehyde and acetic anhydride.

The acetyl compound of salicyl aldehyde, together with sodium acetate are first formed:

$$C_6H_4\begin{cases}ONa\\CHO\end{cases} + \begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!\!>\!O = C_6H_4\begin{cases}O{-}CO{-}CH_3\\CHO\end{cases} + CH_3{-}CO_2Na.$$

The former compound splits out a molecule of water at a high temperature, forming cumarin:*

* We have already had occasion to notice this elimination of water in aldehydes in the case of the artificial production of cinnamaldehyde. It occurs with aromatic compounds only when there are two side-chains in the ortho-position present.

$$C_6H_4\begin{cases}O\text{-}CO\text{-}CH_3\\CHO\end{cases} = C_6H_4\begin{cases}O\text{-}CO\text{-}CH\\CH\end{cases} + H_2O.$$

Cumarin

Cumarin, $C_9H_6O_2$, forms colorless columnar crystals, fusing at 67° and boiling at 290°. It possesses a strong odor, which in the dilute state resembles that of the woodward. When boiled with potassa, it takes up water and is converted into cumaric acid.

By the action of nascent hydrogen, it takes up a molecule of hydrogen and a molecule of water, and is changed into *melilotic acid*, $C_9H_{10}O_3$,

$$C_9H_6O_2 + H_2O + H_2 = C_9H_{10}O_3.$$

Melilotic, or Hydrocumaric Acid stands in the same relation to cumaric acid as hydrocinnamic acid to cinnamic acid. It occurs with cumarin in sweet clover, from which it is obtained. It forms long colorless needles fusing at 82°, which are somewhat soluble in water. On distillation, it splits out water forming the anhydride:

$$C_6H_4\begin{cases}O\text{---------}\\CH_2\text{-}CH_2\text{-}CO\end{cases}$$ *Hydrocumarin.*

Since cumarin can be produced artificially from sodium salicyl aldehyde and acetic anhydride, the homologues of cumarin can also be obtained by taking instead of acetic anhydride, propionic anhydride, butyric anhydride, etc.

From a glucoside (see later) which occurs in coffee, and is called *caffetannic acid*, there is obtained an acid, $C_9H_8O_4 = C_6H_3(OH)_2CH{=}CH\text{-}COOH$, *caffeic acid*, or *dihydroxycinnamic acid*. It crystallizes in yellow leaflets, which are colored grass-green by ferric chloride. Fusing potassium hydroxide converts it into protocatechuic acid, $C_6H_3(OH)_2COOH$, and acetic acid. By the action of nascent hydrogen, it is transformed into *hydrocaffeic acid*, $C_9H_{10}O_4$.

Umbelliferon, $C_9H_6O_3$, contains one more atom of oxygen than cumarin. It exists ready formed in spurge-laurel, and

can be obtained by the distillation of the resins obtained from the umbellifers (gum asafœtida, galbanum, etc.). Its constitution is $C_6H_3\begin{cases}OH\\ -O-\\ CH{=}CH{-}CO\end{cases}$, and its relation to cumarin is the same as that of hydroxybenzoic acid to benzoic acid. It forms prisms fusing at 240° which, when fused with potassium hydroxide, yield resorcinol, $C_6H_4(OH)_2$, and are converted by nascent hydrogen into *hydro-umbellic acid*,

$$C_9H_{10}O_4 = C_6H_3(OH)_2CH_2CH_2COOH,$$

an isomer of hydrocaffeic acid :

$$C_9H_6O_3 + H_2O + H_2 = C_9H_{10}O_4.$$

Daphnetin, $C_9H_6O_4$, which is formed from daphnin, and *aesculetin*, $C_9H_6O_4$, from aesculin, are also to be considered as dioxycumarins. (Compare glucosides.)

Cymene.

There are only a few of the theoretically possible hydrocarbons with ten atoms of carbon known.

1) *Tetramethylbenzene*, $C_6H_2(CH_3)_4$, *durene*, is formed from monobrompseudocumene and methyl iodide. It fuses at 79° and boils at 190°.

2) *Dimethyl-ethyl-benzene*, $C_6H_3(CH_3)_2(C_2H_5)$, is obtained from monobromxylene and ethyl iodide. It boils at 184°.

3) *Di-ethyl-benzene*, $C_6H_4(C_2H_5)_2$, is produced from monobromethylbenzene and ethyl iodide. It boils at 178°.

4) *Methyl-propyl-benzene*, **Cymene**, $C_6H_4\begin{cases}CH_3\\ C_3H_7\end{cases}$, $C_{10}H_{13}$, occurs in nature. It is contained in many essential oils, and is formed when essential oils of the formula $C_{10}H_{16}$, are heated with iodine, or when their dibromides are treated with alcoholic potassa. It is also formed by heating camphor with phosphorus sulphide. It is a liquid boiling at 175°, which yields on oxidation paratoluic and terephthalic acids.

5) *Butylbenzene and Isobutylbenzene*, $C_6H_5{-}C_4H_9$, are formed from brombenzene and the butyl bromides. They are liquids boiling at 180° and 167°.

Thymol is the phenol of cymene, $C_6H_3\begin{cases}1\ OH\\2\ CH_3\\5\ C_3H_7\end{cases} = C_{10}H_{14}O$ Thymol is a constituent of thyme-oil, and crystallizes in thin leaflets with a characteristic odor and burning taste. It fuses at 44° and boils at 230° Among the other derivatives of cymene are:

Cymyl alcohol, $C_6H_4\begin{cases}CH_2{-}OH\\C_3H_7\end{cases}$,

Cumic aldehyde, $C_6H_4\begin{cases}CHO\\C_3H_7\end{cases}$, and

Cumic acid, $C_6H_4\begin{cases}COOH\\C_3H_7\end{cases}$.

Cumic Aldehyde occurs in Roman caraway-oil. The alcohol and acid have been produced from it.

Cymyl Alcohol, or *Cymol*, is a liquid with a pleasant odor boiling at 243°. Cumic aldehyde is an oil with an agreeable odor boiling at 237°. *Cumic Acid* forms long colorless needles, which fuse at 114° and sublime.

The three possible tetracarboxylic acids of benzene are all known. They are obtained from mellitic acid, and are known as *pyromellitic acid*, *phrenitic acid*, and *mellophanic acid*, $C_6H_2(COOH)_4$.

Still less is known about the aromatic hydrocarbons containing twelve atoms of carbon directly united. To this series belongs hexamethylbenzene, $C_6(CH_3)_6$, a body fusing at 150° and boiling at 260°. From it is derived the hexacarboxylic acid, mellitic acid, $C_6(COOH)_6$.

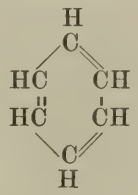
Mellitic Acid, $C_{12}H_6O_{12}$, is found as a mineral, under the name of mellite, or honeystone (aluminum mellitate), in lignite beds. The acid crystallizes in fine needles which fuse on heating, and on distillation break into carbonic acid and pyromellitic acid:

$$C_{12}H_6O_{12} = C_{10}H_6O_8 + 2\ CO_2.$$

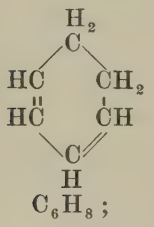
When distilled with lime, it yields benzene and calcium carbonate.

Reduction of the Benzene Derivatives.

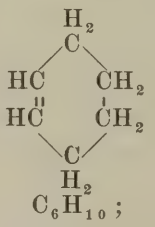
As we have already seen, each carbon atom of the benzene nucleus is united to two other carbon atoms, to one by a single binding, to the other by a double binding.



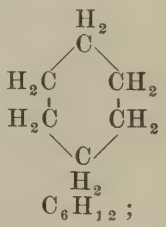
Under the proper conditions, the double bindings can be either partly or wholly dissolved, and bodies thus obtained which are derivatives of the following hydrocarbons :



C_6H_8 ;



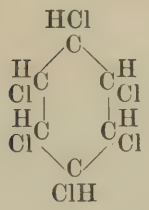
C_6H_{10} ;



C_6H_{12} ;

In all of these cases, however, the benzene nucleus remains unbroken. As yet, the benzene nucleus has not been opened, without the entire molecule breaking up.

The addition of hydrogen to benzene cannot be effected by the action of any reducing agent. Addition products with chlorine, however, are easily produced. When chlorine is led into benzene, benzene hexachloride, $C_6H_6Cl_6$, is formed :

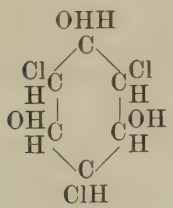


Hypochlorous acid, HClO, acts like chlorine, dissolving the double bindings. If benzene is added to an aqueous solution of hypochlorous acid, a body, $C_6H_9Cl_3O_3$, is produced:

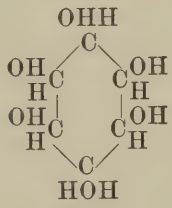
$$C_6H_6 + 3\ HClO = C_6H_9Cl_3O_3,$$

or $C_6H_6Cl_3(OH)_3$. On treatment of this substance with KOH, the three chlorine atoms are replaced by hydroxyls, forming *phenose*, $C_6H_6(OH)_6 = C_6H_{12}O_6$, a body constituted similarly to glucose.

The constitution of these bodies is:



Trichlorphenose



Phenose

Phenose is not fermentable.

Although benzene cannot be reduced by hydrogen, *i.e.* the hydrogen has not the power to dissolve the double bindings of benzene, a reduction takes place when the hydrogen of the nucleus is partly replaced by carboxyl- or methyl-groups. Phthalic acid, for instance, yields three reduction-products (hydrophthalic acids):

Phthalic Acid, $C_6H_4(CO_2H)_2$,
Hydro-phthalic Acid, $C_6H_6(CO_2H)_2$ = Phthalic acid + 2 H
Tetra-hydro-phthalic Acid, $C_6H_8(CO_2H)_2$ = Phthalic acid + 4 H
Hexa-hydro-phthalic Acid, $C_6H_{10}(CO_2H)_2$ = Phthalic acid + 6 H.

Benzoic acid, $C_6H_5{}^-COOH$, yields with sodium amalgam, *hydrobenzoic acid*, $C_6H_9COOH = C_7H_{10}O_2$, which is a volatile acid, liquid at ordinary temperatures, and converted back into benzoic acid by the action of the oxygen of the air.

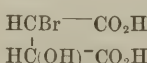
Hydrobenzoic acid is benzoic acid to which four hydrogen atoms have been added:

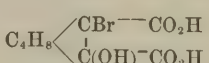
Phthalic acid and terephthalic acid give with sodium amalgam *hydro-phthalic acid* and *hydro-terephthalic acid*, $C_8H_8O_4$. Both are solid compounds, and, as diabasic acids, form two series of salts.

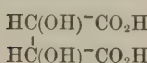
By heating phthalic acid with iodohydric acid (which acts as an energetic reducing agent at a high temperature) to 250°, *hexahydro-phthalic acid*, $C_8H_{12}O_4$, is obtained. By another method (by distillation of hydropyromellitic acid) *tetra-hydro-phthalic acid*, $C_8H_{10}O_4$, has been obtained.

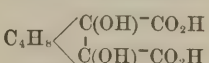
Tetrahydrophthalic acid takes up a molecule of bromine, forming the acid, $C_8H_{10}Br_2O_4$. The bromine atoms in this derivative can be replaced by hydroxyls, yielding *bromo-malo-phthalic acid*, $C_8H_{10}Br(OH)O_4$, and *tartro-phthalic acid*, $C_8H_{10}(OH)_2O_4$.

Both of these acids owe their names to their analogy to brom-malic acid and tartaric acid:

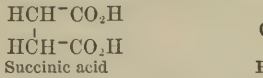

Brommalic acid


Bromomalophthalic acid


Tartaric acid


Tartrophthalic acid

The hexahydrophthalic acid is an analogue of succinic acid.



Succinic acid — Hexahydrophthalic acid

Pyromellitic acid, $C_6H_2(CO_2H)_4 = C_{10}H_6O_8$, is reduced to *hydropyromellitic acid*, $C_{10}H_{12}O_8$, and mellitic acid, $C_6(CO_2H)_6 = C_{12}H_6O_{12}$, to *hydromellitic acid*, $C_{12}H_{12}O_{12}$.

The hydrocarbons derived from benzene act differently on reduction from benzene. The carboxylated benzene takes up enough hydrogen to break all the three double bindings into simple ones, but methylbenzene (toluene) takes up only two atoms of hydrogen, dimethylbenzene (xylene) four, while trimethylbenzene (mesitylene) takes up six.

Benzene,	C_6H_6		
Toluene,	C_7H_8	becomes	C_7H_{10}
Xylene,	C_8H_{10}	becomes	C_8H_{14}
Mesitylene,	C_9H_{12}	becomes	C_9H_{18}

Indigo.

All the benzene derivatives, whose constitution allowed of their introduction into the system, having been considered, we come now to a class of compounds which are very important in technology, and which are so complicated that they cannot well be classified under any of the series which have been explained. They form the *indigo group.*

In various plants (species of indigo, *Isatis tinctoria*, and woad, *Polygonum tinctorium*, etc.), there occurs a substance of a glucoside nature, which, on fermentation or by boiling with acids, is decomposed into sugar and indigo-white. The body which occurs ready formed in plants is called *indican.*

The indigo-white, which is formed from it when exposed to

the air, is, after a time, converted back into *indigo-blue.* The indigo of commerce consists of several substances.

Indigo-Blue, $C_{16}H_{10}N_2O_3$, is obtained in the pure state either by careful sublimation of commercial indigo, or from indigo-white, or by methods which will be mentioned farther on. It is a pure blue, tasteless, odorless powder, which is insoluble in water, alcohol, ether, and dilute acids and alkalis. At 300° it partially decomposes, giving off purplish-red vapors which condense to glittering deep copper-colored prisms. On boiling with potassa and powdered manganese di-oxide, it is converted into anthranilic acid. Distillation with potassium hydroxide resolves it into aniline. Fuming, as well as very concentrated sulphuric acid dissolves it with the formation of sulphonic acids. This solution is used in dyeing. Indigo-blue forms two compounds with sulphuric acid, viz.:

$$C_{16}H_9N_2O_2 . HSO_3,$$

sulphopurpuric acid, and $C_{16}H_8N_2O_2 . 2\,HSO_3$, *indigotindisulphonic acid.* The former is insoluble in dilute acids, the latter soluble. By adding water, therefore, to a solution of indigo-blue in sulphuric acid, the sulphopurpuric acid is precipitated, while the indigotindisulphonic acid remains in solution.

Indigo-blue, when treated with reducing agents (H_2S, $FeSO_4$, etc.), in the presence of alkalis, takes up a molecule of hydrogen, loses its blue color, and is converted into *indigo-white:*

$$C_{16}H_{10}N_2O_2 + H_2 = C_{16}H_{12}N_2O_2.$$

Indigo-white is changed into indigo-blue by exposure to the air. On treating the indigo-blue with stronger reducing agents, however (tin and chlorhydric acid), the reduction goes further, and a yellow body is obtained combined with the tin, which takes up oxygen from the air and becomes red.

On account of its great instability it has not been thoroughly examined. It cannot be converted back into indigo-blue.

Indigo-White, $C_{16}H_{12}N_2O_2$, is yellow, odorless, and tasteless. It is insoluble in water, soluble in alcohol and alkalis.

When indigo-blue is oxidized with nitric or chromic acid, it takes up oxygen and passes into *isatin,* $C_{16}H_{10}N_2O_4$:

$$C_{16}H_{10}N_2O_2 + O_2 = C_{16}H_{10}N_2O_4.$$

Isatin, $C_{16}H_{10}N_2O_4$, or $C_8H_5NO_2$, forms reddish-brown, odorless and bitter prisms, which are slightly soluble in alcohol and water, and easily soluble in alcohol. It fuses on heating, and volatilizes with partial decomposition. Chlorine and bromine yield substitution-products with it; nitric acid destroys it. It is soluble in cold potassa-lye with a violet color. On warming this solution, the isatin takes up a molecule of water, the solution becomes yellow, and the potassium salt of *isatinic acid,* $C_{16}H_{14}N_2O_6$, or $C_8H_7NO_3$, is formed :

$$C_8H_5NO_2 + H_2O = C_8H_7NO_3.$$

On heating isatin with potassium hydroxide, it is decomposed into aniline and carbonic acid :

$$C_8H_5NO_2 + 4\,KOH = C_6H_7N + 2\,K_2CO_3 + H_2.$$

Isatin unites with acid alkali sulphites to form crystalline compounds (we shall see later on that it is a ketone).

Reducing agents act on isatin in two ways, viz., by the addition of hydrogen, and the abstraction of oxygen.

Isatid, $C_{16}H_{12}N_2O_4$, is a dirty-white powder insoluble in water. It is formed by the action of zinc and chlorhydric acid on isatin. It yields substitution-products.

Dioxindole, $C_8H_7NO_2$, is formed from isatin by the action of sodium amalgam. It crystallizes in yellow prisms which are quite easily soluble in hot water. It forms compounds with metals, with which it also yields

substitutions of four atoms of hydrogen. If the reduction of isatin with sodium amalgam takes place in an acid solution, the reduction goes farther, forming

Oxindole, C_8H_7NO. It crystallizes in colorless needles fusing at 120°, is easily soluble in hot water, and can be distilled without decomposition. It yields compounds with metals and with acids.

Indole, C_8H_7N, is formed by the distillation of oxindole over zinc dust. It has the unpleasant odor of excrement, fuses at 52°, is crystalline, and can be distilled with but little decomposition. It colors a slip of pine wood moistened with chlorhydric acid, cherry-red. It occurs in human excrement, and can be obtained also by the decomposition of albumen.

In the urine of mammals, a substance occurs called *indican,* which is *indoxylsulphuric acid,* $C_8H_6N{-}SO_4H$. When moistened with chlorhydric acid and exposed to the air, it yields indigo-blue.

By the reduction of isatin, not, however, by nascent hydrogen, in which case hydrogen adds on, but by abstraction of oxygen, which is effected by a solution of phosphorus in phosphorus chloride, indigo-blue is regenerated.

Indigo-blue and a number of its derivatives have been produced synthetically. *Indole* is formed by leading di-ethyltoluidine through a red-hot tube, and by heating orthonitrocinnamic acid with potassium hydroxide and iron filings. *Oxindole* is obtained by reducing orthonitrophenylacetic acid, $C_6H_4\left\{\begin{matrix}NO_2\\CH_2{-}CO_2H\end{matrix}\right.$, and is the anhydride of amidophenylacetic acid, $C_6H_4\left\{\begin{matrix}NH\\CH_2{-}CO\end{matrix}\right.$. Nitrous acid converts oxindole into *nitroso-oxindole,* $C_6H_4\left\{\begin{matrix}NH\text{———}\\CH(NO){-}CO\end{matrix}\right.$, which on reduction, affords *amido-oxindole,* $C_6H_4\left\{\begin{matrix}NH\text{———}\\CH(NH_2){-}CO\end{matrix}\right.$. Amidooxindole yields on oxidation with ferric chloride, cupric chloride, etc., *isatin,* $C_6H_4\left\{\begin{matrix}NH\\CO{-}CO\end{matrix}\right.$, which by treatment with phosphorus pentachloride gives $C_6H_4\left\{\begin{matrix}NH\\CO{-}CCl_2\end{matrix}\right.$. This compound immediately splits out a molecule of HCl, forming :

$$C_6H_4\begin{cases}N\\ CO\text{-}CCl\end{cases},$$

which gives indigo-blue on reduction. From isatin there are also derived *isatinic acid*, $C_6H_4\begin{cases}NH_2\\ CO\text{-}CO_2H\end{cases}$, and *dioxindole*:

$$C_6H_4\begin{cases}NH\text{---}\\ CH(OH)\text{-}CO\end{cases}.$$

Indole is probably $C_6H_4\begin{cases}NH\\ CH{=}CH\end{cases}$.

By treating orthonitrocinnamic acid with bromine, the dibromide, $C_6H_4\langle\begin{matrix}NO_2\\ CHBr\text{-}CHBr\text{-}CO_2H\end{matrix}$, is produced, which with sodium hydroxide yields *orthonitrophenylpropiolic acid*, $C_6H_4\langle\begin{matrix}NO_2\\ C{\equiv}C\text{-}CO_2H\end{matrix}$. By the action of a weak reducing agent (grape-sugar) on this acid indigo-blue is formed:

$$2\,C_9H_5NO_4 + 2\,H_2 = C_{16}H_{10}N_2O_2 + 2\,H_2O + 2\,CO_2,$$

By the action of sodium hydroxide alone, isatin is formed.

By treating orthonitrophenylpropiolic ethyl ester with concentrated sulphuric acid, it is converted into the isomeric *isatogenic ethyl ester*:

$$C_6H_4\langle\begin{matrix}C{\equiv}C\text{-}CO_2C_2H_5\\ NO_2\end{matrix} = C_6H_4\langle\begin{matrix}C\\ |\\ N\end{matrix}\rangle\begin{matrix}O_2\\ |\\ C\text{-}CO_2C_2H_5\end{matrix}.$$

Owing to its instability the free acid has not been obtained.

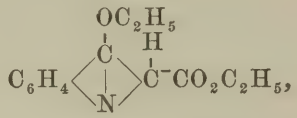
Isatogenic ester on reduction is converted into *indoxylic ethyl ester*:

$$C_6H_4\langle\begin{matrix}C(OH)\\ |\\ N\end{matrix}\rangle\begin{matrix}H\\ |\\ C\text{-}CO_2C_2H_5\end{matrix},$$

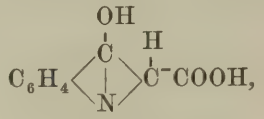
thick, colorless prisms fusing at 120–121°. When heated with

concentrated sulphuric acid, it passes into indigo-sulphonic acid.

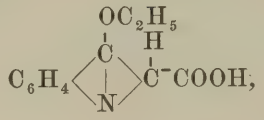
The *ethoxyindoxylic ethyl ester:*



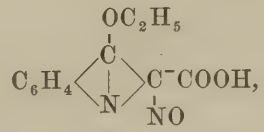
has been obtained in the form of large colorless crystals fusing at 98°. On saponifying indoxylic ethyl ester, *indoxylic acid:*



fusing at 122–123°, is formed. By the action of acid oxidizing agents, it is converted into indigo-blue. By boiling the ester with alcoholic baryta and acidifying, glittering leaflets of *ethoxyindoxylic acid:*

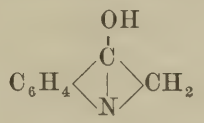


fusing at 160°, are obtained. On warming with a solution of ferric chloride and HCl, it loses its ethyl group and is converted into indigo-blue. The ethoxyindoxylic acid behaves with nitrous acid like oxindole, yielding *ethoxy-nitroso-indoxylic acid:*

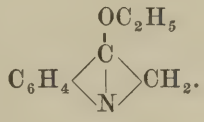


in the form of golden-yellow needles. On reduction, it yields,

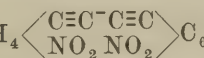
like oxindol, an amido-compound which gives on oxidation, isatin. Indoxylic acid when heated to fusion evolves CO_2, and affords an oil which is probably *indoxyl:*



Ethoxyindoxylic acid, however, also evolves CO_2 on fusion, and yields an oil possessing the odor of indol, which is *ethoxyindoxyl:*



Orthonitrophenylpropiolic acid is converted by boiling with water into *orthonitrophenylacetylene.* By exposing the latter in the form of its cuprous oxide compound to the action of an alkaline solution of potassium ferricyanide, it is changed into *orthodinitrodiphenyldiacetylene:*



which is the dinitro-derivative of the hydrocarbon from which indoxyl is derived, viz., *diacetylenephenyl:*

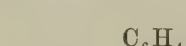
$$C_6H_5{-}C{\equiv}C{-}C{\equiv}C{-}C_6H_5.$$

The dinitro-compound is converted by the action of conc. sulphuric acid into *diisatogen,* $C_{16}H_8N_2O_4$, which by the action of reducing agents is changed into indigo-blue :

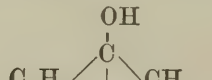
$$C_{16}H_8N_2O_4 - O_2 + H_2 = C_{16}H_{10}N_2O_2.$$

The formation of indigo-blue from orthonitrophenylpro-

piolic acid is, then, dependent on the formation of the intermediate compound, indoxyl :



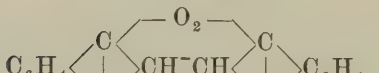
Orthonitrophenylpropiolic acid



Indoxyl

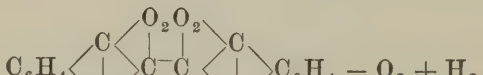


Indigo-white

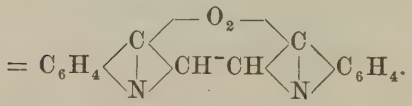


Indigo-blue

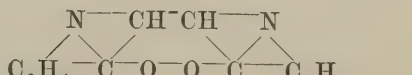
The formation of indigo-blue from diisatogen is probably as follows :



Diisatogen



The constitution of the blue is more apparent when expressed :



Attention has frequently been drawn to the easy substitutibility of the hydrogen of benzene and its derivatives, by other elements and atomic groups. The ease with which the hydrogen of benzene is replaced gives rise to a series of reactions which as yet have not received particular attention. On passing benzene through a red-hot tube, diphenyl, $C_6H_6{}^-C_6H_6$, (p. 204) is formed, *i.e.*, an H of the benzene, is replaced by another benzene rest while hydrogen is set free. Phenol on fusion with potassium hydroxide yields *diphenol*, $\begin{matrix} C_6H_4{}^-OH \\ | \\ C_6H_4{}^-OH \end{matrix}$:

$$2\,C_6H_5OH = C_6H_4(OH)^-C_6H_4(OH) + H_2,$$

and hydrazobenzene, $C_6H_5{}^-NH^-NH^-C_6H_5$, is converted by acids into benzidine, $\begin{matrix} C_6H_4{}^-NH_2 \\ | \\ C_6H_4{}^-NH_2 \end{matrix}$ (p. 224). By the action of methyl chloride, etc., on benzene in presence of aluminum chloride, chlorhydric acid is evolved, the chlorine of the methyl chloride unites with the hydrogen of the benzene, and methylbenzene, dimethylbenzene, etc., up to hexamethylbenzene are formed (p. 275).

When sulphuric acid is allowed to act on a mixture of benzene, phenol, etc., with an aldehyde, the oxygen of the aldehyde unites with the hydrogen of the benzene, forming water and condensation products:

$$CH_3{}^-CHO + 2\,C_6H_6 = H_2O + CH_3{}^-CH\!\left\langle \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} \right.$$

Diphenylethylidene

Acid anhydrides also react on benzene and its derivatives in presence of sulphuric acid, forming condensation products:

$$C_6H_4\!\left\langle \begin{matrix} CO \\ CO \end{matrix} \right\rangle O + 2\,C_6H_5OH = C_6H_4\!\left\langle \begin{matrix} CO \\ C{=}(C_6H_4OH)_2 \end{matrix} \right\rangle O$$

Phenolphthaleïn

The phthaleïns are produced by this method. The most

interesting of these reactions is the condensation of a mixture of aniline and ortho- or paratoluidine or its homologues. Two hydrogen atoms of the methyl and 2 H's of the two benzene rests are oxidized to water, and a triamidoderivative of triphenylmethane is formed :

$$\begin{matrix} C_6H_5NH_2 \\ C_6H_5NH_2 \end{matrix} + C_6H_4\begin{matrix} NH_2 \\ CH_3 \end{matrix} = \begin{matrix} C_6H_4(NH_2) \\ C_6H_4(NH_2) \end{matrix}\!\!>\!C\!<\!\begin{matrix} C_6H_4\text{-}NH_2 \\ H \end{matrix}.$$

This compound is *paraleucaniline*, and is converted at once by further oxidation into the amide :

$$\begin{matrix} C_6H_4(NH_2) \\ C_6H_4(NH_2) \end{matrix}\!\!>\!C\!<\!\begin{matrix} C_6H_4 \\ \text{———} \end{matrix}\!\!>\!NH,$$

or its salts, *pararosaniline* (p. 259).

This condensation and the consequent union of several benzene rests, either directly to each other or indirectly by means of methyl or ethyl rests, also takes place, as we have seen, by exposing benzene and its derivatives to a high heat. It is from this reason that diphenyl and other hydrocarbons which will be mentioned later, as naphthalene, anthracene, phenanthrene, chrysene, etc., exist in coal-tar.

Among the condensation products which have not yet been mentioned are *fluorene*, or *diphenylenemethane*, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!CH_2$, which is found in coal-tar, and has also been produced synthetically. It fuses at 113° and boils at 295°. *Diphenylbenzene*, $C_6H_5\text{-}C_6H_4\text{-}C_6H_5$, which is formed by leading a mixture of benzene and phenol through a heated tube (f. p. 205°), and *carbazol*, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!NH$, which is found in coal-tar. Lastly *acridine*, $C_{12}H_9N$, which is isomeric with carbazol.

Retrospect.

In reviewing the compounds derived from benzene, we are struck by the abundance of isomers which the higher substituted benzenes yield, and also by the differences in the characteristic properties which exist between the substitution-products of the aromatic bodies and those of the fatty series. The aromatic chlorides, bromides, and iodides (so long as the halogen is not in the side-chain), are far more stable than their analogues in the fatty series. The hydroxyl derivatives are more stable than the alcohols, and in many relations resemble acids. Sulphuric and nitric acids convert the aromatic compounds with great ease into sulphonic acids (substitutions of the rest SO_2OH) or sulphones (the rest SO_2) and nitro-compounds (substitutions of the rest NO_2).

The following is a list of the more important derivatives of benzene arranged in series.

Hydroxyl Derivatives.

1. Monohydroxyl derivatives :

$C_6H_5(OH)$, *Phenol.*

2. Dihydroxyl derivatives :

$C_6H_4(OH)_2$, *Resorcinol, Catechol, Quinol.*

3. Trihydroxyl derivatives :

$C_6H_3(OH)_3$, *Pyrogallol, Phloroglucinol.*

The third is not known, nor have any higher hydroxyl derivatives been obtained.

Carboxyl Derivatives.

1. Monocarboxylic acids :

$C_6H_5{}^-CO_2H$, *Benzoic acid.*

2. Dicarboxylic acids :

1) $C_6H_4\begin{cases}1\ CO_2H\\2\ CO_2H,\end{cases}$ *Phthalic acid.*

2) $C_6H_4\begin{cases}1\ CO_2H\\3\ CO_2H,\end{cases}$ *Isophthalic acid.*

3) $C_6H_4\begin{cases}1\ CO_2H\\4\ CO_2H,\end{cases}$ *Terephthalic acid.*

3. Tricarboxylic acids : $C_6H_3(CO_2H)_3$:

1) 1 . 2 . 3. *Hemimellitic acid.*
2) 1 . 2 . 4. *Trimellitic acid.*
3) 1 . 3 . 5. *Trimesinic acid.*

4. Tetracarboxylic acids : $C_6H_2(CO_2H)_4$:

1) *Pyromellitic acid.*
2) *Phrenitic acid.*
3) *Mellophanic acid.*

5. Pentacarboxylic acids : (unknown).
6. Hexacarboxylic acids :

$C_6(CO_2H)_6$, *Mellitic acid.*

In other series are :

1. Phenylformic acid :

$C_6H_5{}^-CO_2H$, *Benzoic acid.*

2. Phenylacetic acid :

$C_6H_5{}^-CH_2CO_2H$, *Alphatoluic acid.*

3. Phenylglycollic acid :

$C_6H_5{}^-CH(OH)CO_2H$, *Mandelic acid.*

4. Phenylpropionic acid :

$C_6H_5{-}CH_2{-}CH_2{-}CO_2H$, *Hydrocinnamic acid.*

5. Phenylacrylic acid :

$C_6H_5{-}CH{=}CH{-}CO_2H$, *Cinnamic acid.*

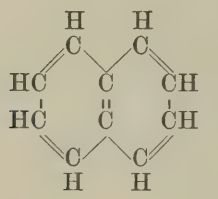
Hydrocarbons.

1.	Benzene, C_6H_6,	B. p.	82°.
2.	Methylbenzene, toluene, $C_6H_5CH_3 = C_7H_8$,	"	111°.
3.	Ethylbenzene, $C_6H_5{-}C_2H_5 = C_8H_{10}$,	"	134°.
4.	Propylbenzene, $C_6H_5{-}C_3H_7 = C_9H_{12}$,	"	157°.
	Isopropylbenzene, cumene, $C_6H_5{-}C_3H_7$,	"	151°.
5.	Butylbenzene, $C_6H_5{-}C_4H_9 = C_{10}H_{14}$,	"	180°.
	Isobutylbenzene, $C_6H_5{-}C_4H_9$,	"	167°.
6.	Amylbenzene, $C_6H_5{-}C_5H_{11} = C_{11}H_{16}$,	"	193°.
7.	Dimethylbenzene, xylene, $C_6H_4(CH_3)_2 = C_8H_{10}$,	"	140°.
8.	Methylethylbenzene, $C_6H_5(C_2H_5)(CH_3)$,	"	160°.
9.	Methylpropylbenzene, cymene, $C_6H_4(CH_3)(C_3H_7) = C_9H_{12}$,	"	175°.
10.	Diethylbenzene, $C_6H_4(C_2H_5)_2 = C_{10}H_{14}$,	"	178°.
11.	Methylamylbenzene, $C_6H_4(CH_3)(C_5H_{11}) = C_{12}H_{18}$,	"	213°.
12.	Trimethylbenzene,* $C_6H_3(CH_3)_3 = C_9H_{12}$,	"	166°.
13.	Dimethylethylbenzene, ethylxylene, $C_6H_3(CH_3)_2(C_2H_5) = C_{10}H_{14}$,	"	184°.
14.	Dimethylamylbenzene, amylxylene, $C_6H_3(CH_3)_2C_5H_{11} = C_{13}H_{20}$,	"	233°.

* Mesitylene and the pseudocumene of coal-tar.

Naphthalene.

There is found in coal-tar, besides benzene and its methyl-substitutions, a very large amount of another hydrocarbon which is always formed when organic substances, even of the simplest constitution, as alcohol, acetic acid, etc., are exposed to a red heat in the absence of air. This body is *naphthalene*, $C_{10}H_8$, a derivative of benzene, and of the following constitution:



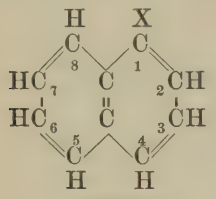
$$\begin{array}{l} CH{=}CH{-}C{-}CH{=}CH \\ | \qquad\quad \| \qquad | \\ CH{=}CH{-}C{-}CH{=}CH \end{array}$$

It is a benzene nucleus in which two adjacent hydrogen atoms are replaced by the divalent hydrocarbon rest, C_4H_4, or $^{-}CH{=}CH{-}CH{=}CH^{-}$.

This hydrocarbon rest is a part of a benzene ring which, when attached to another benzene ring, produces a double ring. The formula of naphthalene is represented by a double benzene nucleus, or it might be said by two benzene rings welded together. We see at once that naphthalene is capable of yielding an immense number of substitutions, and that the number of isomeric derivatives must be greater than in the case of benzene. We shall only take up a few of the more important derivatives.

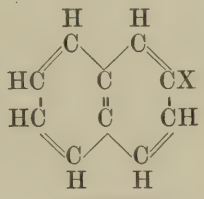
Naphthalene yields two series of mono-substitutions depend-

ing on whether the hydrogen atom which is replaced is adjacent or not to the carbon atoms which do not bind hydrogen. If the substituting element be represented by X, the constitution of the two isomers will be :



α Compound

and



β Compound

When two atoms of hydrogen in naphthalene are replaced by other elements, or groups, there are altogether ten isomers possible. Four of these isomers are produced by substitutions in only one half of the double ring. Most of the isomers known at present belong to this class. When the substitution takes place in both halves of the double ring there are six more isomers possible. Representing the eight atoms of hydrogen in the naphthalene by figures, we have the following isomers :

Mono-substitutions : 1) $C_{10}H_7 . 1\,X$, or $C_{10}H_7 . 4\,X$
2) $C_{10}H_7 . 2\,X$, or $C_{10}H_7 . 3\,X$

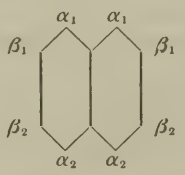
Di-substitutions : 1) $C_{10}H_6 . 1.2\,X_2$
2) $C_{10}H_6 . 1.3\,X_2$
3) $C_{10}H_6 . 1.4\,X_2$
4) $C_{10}H_6 . 2.3\,X_2$

and 5) $C_{10}H_6 . 1.5\,X_2$; 6) $C_{10}H_6 . 1.6\,X_2$;
7) $C_{10}H_6 . 1.7\,X_2$; 8) $C_{10}H_6 . 1.8\,X_2$;
9) $C_{10}H_6 . 2.6\,X_2$; 10) $C_{10}H_6 . 2.7\,X_2$.

In the case of tri-substitutions of naphthalene, there are, when the substitution takes place in only one half of the double ring and the substituting atoms are all the same, two

isomers possible, viz., 1 . 2 . 3 and 1 . 2 . 4. Under the same limitations, there is only one tetra-substitution possible.

The most practical method in use for representing the constitution of the naphthalene derivatives is the following. By lettering the double ring of naphthalene as below :



isomers can easily be indicated. If a di-substitution takes place in one ring, it is expressed by connecting the letters representing the positions of the substituting atoms by a single stroke. If the substitutions are in different rings, the letters are connected by a double stroke. Thus the di-substitutions, Nos. 1 and 6 (see above), would be represented $\alpha_1 - \beta_1$ and $\alpha_1 = \beta_2$. The tri-substitution 1 . 2 . 5 would be $\alpha_1 - \beta_1 = \alpha_2$.

Naphthalene, $C_{10}H_8$, crystallizes in white, rhombic leaflets with a peculiar odor and burning taste. It fuses at 79° and boils at 218°, is insoluble in water, and soluble in alcohol and ether. On oxidation it is converted into oxalic and phthalic acids (p. 263) :

$$C_{10}H_8 + 4\,O_2 = \underset{\text{Oxalic acid}}{C_2H_2O_4} + \underset{\text{Phthalic acid}}{C_8H_6O_4}.$$

The first action of chlorine on naphthalene is to break the double binding of the carbon atoms on one side of the double ring, forming addition-products, after which it produces substitution-products. The following chlorine derivatives are known, a number of them being, however, obtained by other methods.

Naphthalene dichloride, $C_{10}H_8Cl_2$ is a liquid insoluble in water. On heating it splits out a molecule of HCl, and is converted into *monochlor-naphthalene*.

Naphthalene tetrachloride, $C_{10}H_8Cl_4$, crystallizes in large rhombohe-

drons fusing at 182°. On distillation it breaks into *dichlornaphthalene* and chlorhydric acid.

α-Monochlornaphthlene, $C_{10}H_7Cl$, is produced from naphthalene dichloride. It is a colorless oily liquid boiling at 255°.

β-Monochlornaphthalene, $C_{10}H_7Cl$, is obtained by the action of phosphorus pentachloride on β-naphthol. It is crystalline, and fuses at 61° and boils at 256°.

Monochlornaphthalene tetrachloride, $C_{10}H_7Cl \cdot Cl_4$, forms prismatic crystals fusing at 130°, which on distillation break into trichlornaphthalene.

Dichlornaphthalene, $C_{10}H_6Cl_2$, is known in seven isomers, which are chiefly distinguishable by their fusing points and crystalline forms.

Trichlornaphthalene, $C_{10}H_5Cl_3$, exists in four isomers.

Tetrachlornaphthalene, $C_{10}H_4Cl_4$, forms needles fusing at 130°.

Tetrachlornaphthalene is the final product of the action of chlorine on naphthalene, just as naphthalene tetrachloride is the final addition-product of chlorine with naphthalene.

The same solution of the double binding of the carbon atoms (on one side of the double ring) can be effected by hydrogen. When naphthalene is heated with iodohydric acid at 250° with the addition of phosphorus, naphthalene tetrahydride, $C_{10}H_{12}$, an oily liquid boiling at 205°, is obtained.

Finally a *perchlornaphthalene*, $C_{10}Cl_8$, has been obtained by the action of chlorine on naphthalene in the presence of antimony pentachloride. It fuses at 135°.

Bromine acts on naphthalene like chlorine, except that it does not form addition-products so easily. The following derivatives are known :

Bromnaphthalene, $C_{10}H_7Br$, an oil boiling at 277°. The β-compound fuses at 68°.

Dibromnaphthalene, $C_{10}H_6Br_2$, is known in two isomers, one fusing at 81°, the other at 127°.

Tribromnaphthalene, $C_{10}H_5Br_3$, fuses at 75°.

Tetrabromnaphthalene, $C_{10}H_4Br_4$.

With nitric acid the following nitro-compounds are obtained :

Nitronaphthalene, $C_{10}H_7(NO_2)$, yellow, rhombic crystals fusing at 61°.

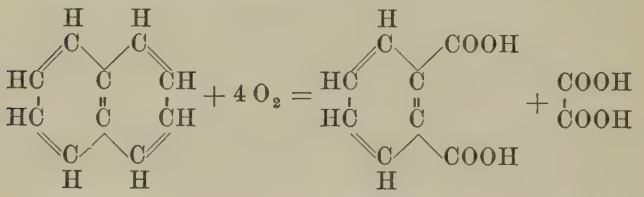
Dinitronaphthalene, $C_{10}H_6(NO_2)_2$. Two isomers are known, one fusing at 214°, the other at 170°.

Trinitronaphthalene, $C_{10}H_5(NO_2)_3$, has been obtained in three modifications. The α-compound forms large leaflets fusing at 122°; the β-compound small crystals fusing at 218°; the γ-compound, needles fusing at 147°.

Tetranitronaphthalene, $C_{10}H_4(NO_2)_4$, needles fusing at 200°.

Nitric acid not only acts on naphthalene as a substituting agent, but also as an oxidizing agent. One side of the double ring of naphthalene breaks, and two carbon atoms split off, while the other two remain united to the benzene nucleus, and are oxidized to carboxyl groups. The dicarboxylic acid thus formed is phthalic acid.

Oxalic acid is also produced besides the phthalic acid :



By the action of nascent hydrogen, the nitronaphthalenes are reduced to amidonaphthalenes (see later). On heating nitronaphthalene with zinc dust, azonaphthalene :

$$C_{10}H_7{-}N{=}N{-}C_{10}H_7,$$

is obtained.

α-Naphthalenesulphonic Acid, $C_{10}H_7{-}SO_3H$, is the chief product of the action of sulphuric acid on naphthalene at a low temperature (80°). It forms a deliquescent, crystalline mass which, by heating with water to 200°, falls into sulphuric acid and naphthalene :

$$C_{10}H_7{-}SO_3H + H_2O = C_{10}H_8 + H_2SO_4.$$

It is a monobasic acid. Its lead salt burns on heating with a smoky flame.

β-Naphthalenesulphonic Acid, $C_{10}H_7{}^-SO_3H$, is formed at a higher temperature (160°). It crystallizes in non-deliquescent crystals which do not decompose on heating with water. Its lead salt glows on heating like tinder.

Naphthalenedisulphonic acid, $C_{10}H_6(SO_3H)_2$, is formed in two modifications by heating naphthalene with an excess of sulphuric acid at 160°.

These sulphonic acids give with chlorine and nitric acid further substitution-products.

When naphthalene is heated with fuming sulphuric acid and phosphoric anhydride, *naphthalenetetrasulphonic acid*, $C_{10}H_4(SO_3H)_4$, is obtained.

On fusion with potassium hydroxide, the naphthalene sulphonic acids exchange the sulpho-group for OH, forming potassium sulphite and the hydroxyl derivatives of naphthalene. The latter are called *naphthols*.

$$C_{10}H_7{}^-SO_3H + 2\,KOH = C_{10}H_7{}^-OH + K_2SO_3 + H_2O.$$

$$C_{10}H_6{}^-(SO_3H)_2 + 4\,KOH = C_{10}H_6(OH)_2 + 2\,K_2SO_3 + 2\,H_2O.$$

α-Naphthol, $C_{10}H_7(OH)$, is obtained from α-naphthalenesulphonic acid. It forms white needles fusing at 94° and distilling at 280°.

β-Naphthol, $C_{10}H_7(OH)$, is obtained from the β-naphthalenesulphonic acid. It forms white leaflets fusing at 122°.

The ethers, nitro-derivatives, and sulphonic acids of both naphthols have been examined. One of the dinitro α-naphthols is a yellow dye (naphthalene yellow), and is met with in commerce.

Dihydroxynaphthalenes, $C_{10}H_6(OH)_2$. Two are known. One is made by heating naphthoquinone with iodohydric acid and phosphorus. It forms colorless needles fusing at 176°. The other is obtained by fusing potassium α-naphthalenedisulphonate with potassium hydroxide. It crystallizes in broad leaflets fusing at 186, and subliming at 160° in needles.

By fusing the potassium β-naphthalenedisulphonate with potassium hydroxide, only potassium β-naphtholsulphonate is obtained.

A *trihydroxynaphthalene*, obtained by the reduction of hydroxynaphthoquinone, is also known.

The characteristic properties of the naphthols correspond completely with those of the phenols.

Naphthoquinone, $C_{10}H_6O_2$, corresponds to quinone, $C_6H_4O_2$, which is derived from benzene.

Naphthoquinone, $C_{10}H_6O_2$, crystallizes in yellow leaflets or needles fusing at 125° and soluble in alcohol, ether, and glacial acetic acid.

Dichlornaphthoquinone, $C_{10}H_4Cl_2O_2$, is obtained by the action of potassium chlorate on naphthalene yellow, (dinitronaphthol). It forms golden-yellow needles insoluble in water, and fusing at 189°. By reduction with sulphurous acid, it is converted into *dichlornaphthoquinol* $C_{10}H_4Cl_2(OH)_2$, (like quinone into quinol, p. 213). This body crystallizes in reddish needles fusing at 140°. By the action of alkalis, the chlorine of dichlornaphthoquinone is replaced by hydroxyl, giving rise to two compounds, $C_{10}H_4Cl(OH)O_2$, *chloroxynaphthalic acid*, and $C_{10}H_4(OH)_2O_2$, *naphthazarin*. We shall meet later on a body which has a similar constitution, and which plays an important part in commerce, viz., *alizarin*.

By the action of phosphorus pentachloride, dichlornaphthoquinone is converted into *pentachlornaphthalene*. $C_{10}H_3Cl_5$. In this case the substitution has advanced to half of the double ring.

When naphthalenesulphonic acid is mixed with potassium cyanide and submitted to dry distillation, *cyannaphthalene*, $C_{10}H_7{}^-CN$, is obtained :

$$C_{10}H_7{}^-SO_3K + KCN = C_{10}H_7{}^-CN + K_2SO_3.$$

The α-cyannaphthalene obtained from potassium α-naphthalenesulphonate is a crystalline substance fusing at 37° and boiling at 298°. When once melted, it remains liquid for a long time. β-cyannaphthalene, produced from potassium β-naphthalenesulphonate, fuses at 66° and boils at 305°. On boiling with potassa, both cyanides are converted into the corresponding carboxylic acids :

$$C_{10}H_7CN + 2H_2O = C_{10}H_7{}^-CO_2H + NH_3.$$

α-cyannaphthalene yields α-naphthoic acid, $C_{10}H_7{}^-CO_2H$, which crystallizes in white needles fusing at 160°.

β-cyannaphthalene yields β-naphthoic acid, which forms needles fusing at 184°. Both are monobasic acids, and their salts also show isomerism.

Dicyannaphthalenes, $C_{10}H_6(CN)_2$, are produced in different ways. Four are known.

α-, β-, γ-, and *δ-Dicyannaphthalenes.* From these four compounds, the four dicarboxylic acids, *α-, β-, γ-,* and *δ-naphthalenedicarboxylic acids* are obtained, $C_{10}H_6(CO_2H)_2$.

By reduction of the nitronaphthalenes, *amidonaphthalenes* are formed.

Mononitronaphthalene yields *amidonaphthalene,* or *naphthalidine,* $C_{10}H_7{}^-NH_2$. The two dinitronaphthalenes yield two diamidonaphthalenes, $C_{10}H_6(NH_2)_2$. Trinitronaphthalene gives a *triamidonaphthalene,* $C_{10}H_5(NH_2)_3$. All of these amines are bases and form finely crystallizable salts with acids.

Naphthalene can be reduced like the benzene derivatives, *i.e.*, it can take up hydrogen. In this case, however, the double bindings of only half the double ring are dissolved, the naphthalene taking up two or four atoms of hydrogen, and forming $C_{10}H_{10}$ or $C_{10}H_{12}$ (see p. 276).

Hypochlorous acids also form double compounds in one half of the double ring, viz.:

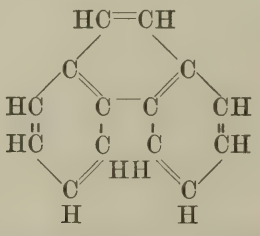
$$C_{10}H_{10}Cl_2O_2 = C_{10}H_8Cl_2(OH)_2,$$
$$C_{10}H_8 + 2\,HOCl = C_{10}H_{10}Cl_2O_2.$$

These, when treated with potassa, exchange their chlorine atoms for hydroxyl, forming napthene alcohol, $C_{10}H_8(OH)_4$ (see p. 277).

Coal-tar contains, besides naphthalene, methylnaphthalene, $C_{10}H_7{}^-CH_3$, *Dimethylnaphthalene,* etc., probably in several isomeric modifications.

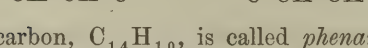
Naphthalene is an example of a peculiar continuation, or duplication, of the benzene nucleus, or ring. It is possible to make a number of similar additions, to the benzene nucleus.

The benzene ring consists of three pairs of doubly bound carbon atoms (C=C), of which one pair unites with the rest, C_4H_4, to form napthalene. When the hydrogen of a second pair is replaced by the rest, $C_4H_4{=}$, a compound results of the following structure :

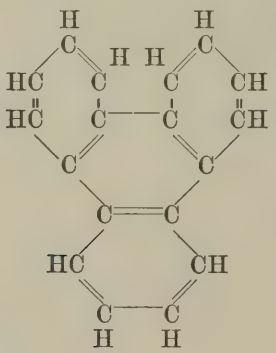


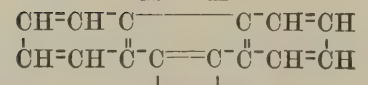


or

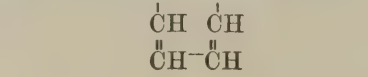


This hydrocarbon, $C_{14}H_{10}$, is called *phenanthrene.* The third pair of carbon atoms can also take up the rest, C_4H_4, forming, $C_{18}H_{12}$, *chrysene :*





or



It is not known whether this species of welding of benzene rings takes place still further. A higher hydrocarbon, *picene*, $C_{22}H_{14}$, is known, but its constitution has not been ascertained.

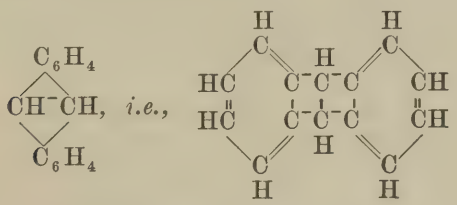
Phenanthrene, $C_{14}H_{10}$, like benzene and naphthalene, is a constituent of coal-tar. It can also be produced synthetically by passing the vapors of stilbene (p. 239) through a strongly heated tube. It crystallizes in leaflets fusing at 100° and boiling at 340°. On oxidation it is converted into the *quinone*, $C_{14}H_8O_2$, and finally into a dicarboxylic acid, *diphenic acid*, or *diphenyldicarboxylic acid*, $C_{14}H_{10}O_4 = C_{12}H_8(CO_2H)_2$. This diphenic acid can be converted into diphenyl:

$$C_6H_5{-}C_6H_5$$

(see p. 204).

Anthracene, $C_{14}H_{10}$, which is also a constituent of coal-tar, is an isomer of phenanthrene. It can be produced synthetically by heating benzoyl chloride with water at 180°, or by the action of sodium on orthobrombenzyl bromide. It crystallizes in white leaflets fusing at 213°.

The constitution of anthracene is:



or

$$\begin{array}{l} CH{-}CH{=}C{-}CH{-}C{=}CH{-}CH \\ CH{-}CH{=}C{-}CH{-}C{=}CH{-}CH \end{array}$$

Anthracene differs from phenanthrene in not being a diphenyl derivative. Phenanthrene is ethylene, in which two atoms of hydrogen are replaced by the di-valent diphenyl rest.

Anthracene, however, is ethane in which four hydrogen atoms have been replaced by the two di-valent benzene rests :

$$\text{Phenanthrene is } \begin{matrix} C_6H_4{-}CH \\ | \quad\quad \| \\ C_6H_4{-}CH \end{matrix};$$

$$\text{Anthracene is } C_6H_4\begin{matrix} \diagup CH \\ \diagdown CH \end{matrix}\!\!>\!C_6H_4.$$

Chlorine converts anthracene into *anthracene dichloride*, $C_{14}H_{10}Cl_2$. With bromine a compound is formed which is both an addition- and substitution-product, *dibromanthracene-tetrabromide*, $C_{14}H_8Br_2 . Br_4$. With carbonyl chloride, $COCl_2$ (p. 35), anthracene yields *anthracene-carboxylic acid*, $C_{14}H_9CO_2H$.

$$C_{14}H_{10} + COCl_2 + H_2O = C_{14}H_9(CO_2H) + 2\,HCl.$$

The quinone of anthracene, anthraquinone, and its derivatives, are the most important compounds of the anthracene series.

When anthracene is heated with nitric acid, *anthraquinone :*

$$C_6H_4\begin{matrix} \diagup CO \\ \diagdown CO \end{matrix}\!\!>\!C_6H_4,$$

is produced. It forms crystals fusing at 277°.

Anthraquinone forms, when treated with sulphuric acid, *anthraquinondisulphonic acid*, $C_{14}H_7O_2(SO_3H)$. The potassium or sodium salt of this acid yields, when fused with potassium hydroxide, *dioxyanthraquinone*, or *alizarin*, $C_{14}H_6(OH)_2O_2 = C_{14}H_8O_4$. The same reaction takes place with the dibromanthraquinone.

Alizarin, $C_{14}H_8O_4$, like indigo-blue, is a coloring matter which does not occur already formed in plants, but is produced from a glucoside contained in them by a species of fermentation. In the root of the madder (*Rubia tinctorium*) a substance occurs which is called *ruberythric acid*, $C_{26}H_{28}O_{14}$. By the action of ferments, or by boiling with dilute acids or alkalis, it falls into glucose and alizarin :

$$C_{26}H_{28}O_{14} + 2\,H_2O = 2\,C_6H_{12}O_6 + C_{14}H_8O_4.$$

Alizarin crystallizes in yellowish-red prisms containing

$3\,H_2O$. At 100°, it loses its water of crystallization, turning red, and at a stronger heat, sublimes in red needles. It is insoluble in water, and difficultly in alcohol and ether, with a yellow color. It is easily soluble in alkalis, with a purplish red color, the solution showing a fine fluorescence. Concentrated sulphuric acid dissolves it without change, forming a red solution which is precipitated by water. Nascent hydrogen converts it into *hydroalizarin*, $C_{14}H_{10}O_4$, and nitric acid into a nitro-derivative.

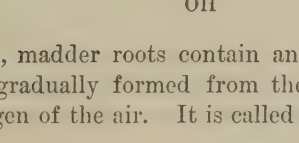
Alizarin has decided acid properties, and unites with bases. To this property it owes its solubility in alkalis. Its compounds with the alkaline earths, alumina and iron oxides, are insoluble. Alizarin, is therefore, precipitated from its solution in alkalis by these substances. In turkey-red dyeing, the alumina compound of alizarin is formed by passing the cloth saturated (mordanted) with an alum solution through a solution of alizarin, the insoluble compound being thus produced directly on the fibre.

On heating with zinc dust, alizarin is reduced to anthracene.

On heating nitroalizarin with glycerol and sulphuric acid, a peculiar reduction takes place with the formation of "*alizarin-blue.*"

$$C_{14}H_7O_4(NO_2) + C_3H_8O_3 = C_{17}H_{19}NO_4 + 3\,H_2O + O_2.$$

The constitution of this compound is:



Besides alizarin, madder roots contain an oxidized alizarin which has been gradually formed from the alizarin by the action of the oxygen of the air. It is called *purpurin:*

$$C_{14}H_5(OH_3)_3O_2 = C_{14}H_8O_5.$$

It is also produced as a side-product in the manufacture of artificial alizarin. Purpurin is soluble in water and alkalis. Its alumina compound is also soluble. It dyes wool, etc., a color resembling that given by alizarin.

In the artificial production of alizarin, there are also two acids obtained which are isomeric with alizarin, viz., *anthraflavic acid*, forming yellow silky needles fusing above 330°, and *isanthraflavic acid*, also forming yellow needles fusing at 330°, but crystallizing with one molecule of H_2O.

From the bark of a species of alder (*Rhamnus frangula*) a glucoside, *frangulin*, $C_{20}H_{20}O_{10}$, is obtained, which on boiling with acids breaks into dextrose and

Frangulic acid, $C_{14}H_8O_4$, which is isomeric with alizarin. It forms crystalline needles containing $\frac{1}{2}$ molecule H_2O, and fuses at 252°.

Besides the above mentioned dioxyanthraquinones, there are *quinazarin*, yellowish-red leaflets fusing at 195°, *purpuroxanthin*, yellowish-red needles fusing at 262°, and *chrysazin*, leaflets fusing at 191°.

Compounds isomeric with purpurin are also known, viz., *anthrapurpurin*, $C_{14}H_8O_5$, orange leaflets fusing over 330°, and *flavopurpurin*, long, golden-yellow needles.

Higher hydroxylated anthraquinones are also known. *Anthrachrysone*, $C_{14}H_8O_6$, golden-yellow, fine needles; *rufiopin*, $C_{14}H_8O_6$, golden-yellow needles; *rufigallic acid*:

$$C_{14}H_3O_8 + 2\,H_2O,$$

small, glittering, brownish-red needles.

The roots of the rhubarb contain a yellow dye-stuff called *chrysophanic acid*, $C_{15}H_{10}O_4$. It does not exist already formed in the plant, but is produced by a species of fermentation from a glucoside, *chrysophan*, $C_{27}H_{30}O_{14}$, which breaks into dextrose and the coloring matter.

Chrysene, $C_{18}H_{12}$ (p. 300), exists in coal tar, from which it

distils at a red heat. It crystallizes in colorless leaflets, fusing at 250°. It is usually more or less yellow. Chlorine, bromine, and nitric acid convert it into substitution products. Chromic acid oxidizes it to *chrysoquinone*, $C_{18}H_{10}O_2$, which can be converted into *chrysoquinol*, $C_{18}H_{10}(OH)_2$, *dichlorchrysoquinone*, $C_{18}H_8Cl_2O_2$, and *perchlorchrysoquinone*, $C_{18}Cl_{10}O_2$. Another hydrocarbon, *retene*, $C_{18}H_{18}$, is also found in coal-tar. It forms mother-of-pearl leaflets fusing at 98°.

Among the other constituents of coal-tar, are *fluoranthrene*, $C_{15}H_{10}$, leaflets fusing at 109°, and *pyrene*, $C_{16}H_{10}$. Both of them yield chlorine, bromine and nitro-derivatives, as well as the quinones and their derivatives. The constitution of fluoranthrene is probably :

$$CH_2\begin{cases}C_6H_3\text{-}CH\\ C_6H_3\text{-}CH\end{cases}$$

and that of pyrene :

$$\begin{matrix}CH\text{-}C_6H_3\text{-}CH\\ \|\qquad\qquad\|\\ CH\text{-}C_6H_3\text{-}CH\end{matrix}$$

In lignite coal-tar, a hydrocarbon, *picene*, $C_{22}H_{14}$, has been found, which crystallizes in colorless leaflets.

Following the compounds which we have so far considered, there are several groups of bodies, the constitution of which has either not yet been determined, or does not allow of their consideration in the groups already treated of, without separating bodies which are really closely related.

Camphor Group.

In the cavities in old stems of a species of trees growing on the islands of Sumatra and Borneo (*Dryobalanops camphora*),

a body is found, which is known as *Borneo-camphor*, or *Borneol*, $C_{10}H_{18}O$. It is crystalline, fuses at 198°, and boils at 212°. It has a burning taste and the peculiar odor of camphor. It is insoluble in water, and turns the plane of polarized light to the right. With chlorhydric acid, it yields a chloride, $C_{10}H_{17}Cl$, and with other acids, ether-like derivatives are formed. Nitric acid converts it into ordinary camphor.

Camphor, $C_{10}H_{16}O$, is found in the camphor-tree, which is indigenous to China and Japan. It forms white, translucent masses with a peculiar odor and a burning taste. It fuses at 175° and boils at 205°. It can be cut with a knife, but is difficult to pulverize. This is accomplished more easily, however, when moistened with alcohol. It is insoluble in water, and soluble in alcohol, ether, acetic acid, concentrated sulphuric and chlorhydric acids. Small particles of it when thrown on water swim on the surface with a rotary motion. It burns, on heating, with a smoky flame. Its alcoholic solution turns the plane of polarized light to the right.

It unites with bromine, forming an addition-product, $C_{10}H_{16}Br_2O$, which on distillation loses bromine, and is converted into *monobromcamphor*. Dehydrating agents, as phosphoric anhydride, zinc chloride, etc., convert it into cymene, (methylpropylbenzene), attacking it, however, more vitally and forming at the same time methylbenzene (toluene), dimethylbenzene (xylene), and trimethylbenzene (pseudocumene).

On digestion with potassa at 300°, it is changed into *campholic acid*, $C_{10}H_{18}O_2$:

$$C_{10}H_{16}O + H_2O = C_{10}H_{18}O_2.$$

By boiling a considerable time with nitric acid, it is converted into *camphoric acid*, $C_{10}H_{16}O_4$.

By the action of sodium, it is changed into *Borneo-camphor*, $C_{10}H_{18}O$. The sodium compound of both Borneo-camphor and ordinary camphor is first formed :

$$2\,C_{10}H_{16}O + Na_2 = C_{10}H_{17}NaO + C_{10}H_{15}NaO.$$

The former being converted by the action of carbonic acid and water into Borneo-camphor.

$$C_{10}H_{17}NaO + CO_2 + H_2O = C_{10}H_{18}O + NaHCO_3.$$

Calcium camphorate, on distillation, is converted into a compound isomeric with phoron, $C_9H_{14}O$ (see later), which by oxidation breaks into acetic acid, $C_2H_4O_2$, *adipinic acid*, $C_6H_{10}O_4$, and carbonic acid :

$$C_9H_{14}O + 7\,O = C_2H_4O_2 + C_6H_{10}O_4 + CO_2.$$

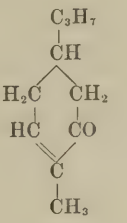
By heating with iodine, camphor is converted into *cumic phenol :*

$$C_{10}H_{13}{}^{-}OH = C_6H_4(C_3H_7){}^{-}CH_2OH,$$

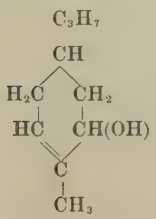
a thick oil isomeric with thymol.

From the above facts the constitution of camphor and its derivatives is most probably as follows :

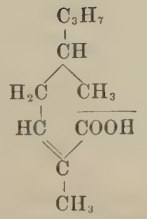
Camphor contains a reduced benzene nucleus with a methyl and a propyl group :



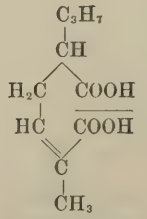
From which are derived :



Borneo-camphor



Campholic acid



Camphoric acid

Several bodies are known which are isomeric with camphor. There are also a large number of substances resembling camphor, of which we shall only mention the following :

Peppermint-camphor, or *menthol*, $C_{10}H_{20}O$, separates from peppermint-oil. It fuses at 42° and boils at 212°, and has the odor and taste of peppermint-oil.

Elecampane-camphor, $C_{10}H_{16}O$, is contained in the roots of the *Inula helenium*. It fuses at 64°. *Helenine*, $C_{12}H_{16}O_2$, occurs with it forming needles fusing at 110°.

The young stems of the dryabalanops, from which Borneo-camphor is obtained, yield also a hydrocarbon, $C_{10}H_{16}$, *camphor-oil*, from which Borneo-camphor seems to be formed after a time.

Essential Oils.

There are a very large number of substances which have the composition $C_{10}H_{16}$. They are called *essential oils*, and occur in plants, being obtained by distilling them with steam. We shall only mention the more important ones. Their constitution is not known with certainty.

In general we understand under essential oils, a number of plant-principles which boil without decomposition, are all indifferent, possess strong odors and burning tastes, are nearly insoluble in water, are mostly liquid and seldom solid at ordinary temperatures, and differ from the fatty oils (glycerides) by their volatility and odors.

They are divided into

1) Essential oils free from oxygen.

These are the essential oils proper. They nearly all possess the composition $C_{10}H_{16}$ (or a multiple of it), are lighter than water, turn the plane of polarized light, and are converted into terephthalic acid by oxidizing agents.

In this class belong *turpentine-oil*, *lemon-oil*, *orange-peel-oil*, *cubeb-oil*, *cardamon-oil*, *savin-oil*, *bergamot-oil*, *cajeput-oil*, *lavender-oil*, *rosemary-oil*, and *amber-oil*.

2) Essential oils containing oxygen.

a) Mixtures of oils containing oxygen with oils free from oxygen: *Valerian-oil, flag-oil, caraway-oil, nutmeg-oil, clove-oil, thyme-oil, parsley-oil, wormwood-oil, rue-oil, curled-mint-oil, peppermint-oil,* and *rose-oil.*

b) Oils containing oxygen:

Bitter almond-oil, cinnamon-oil, anise-oil, fennel-oil, marjoram-oil, camomile-oil, sage-oil, and *tansy-oil.*

3) Oils containing sulphur:

Mustard-oil, spoonwort-oil, and *leek-oil.*

Turpentine-Oil, $C_{10}H_{16}$. Turpentine-oil is the representative of all of the essential oils free from oxygen. Most of its reactions resemble those of the other essential oils of this class.

When incisions are made in the bark of trees belonging to the *abietineæ* family, a thick sap flows out, which is called turpentine, and is a mixture of rosin and turpentine-oil. By distilling with steam, this product yields turpentine-oil.

It is a colorless liquid with a peculiar and disagreeable odor. It boils at 160°, and is lighter than water (sp. gr. 0.86). It is insoluble in water, although it imparts its odor to it. In alcohol, ether, and acetic acid it is soluble. Phosphorus, sulphur, resins, and caoutchouc dissolve in it, and it is hence used in the preparation of resin and oil varnishes. It turns the plane of polarized light, the various kinds having different powers of rotation, by which they can be distinguished. The German oil, from *Pinus sylvestris* and *Abies excelsa*, the French oil, from *Pinus maritima*, and the Venetian oil, from *Larix Europæ*, polarize to the left, the English oil, from *Pinus australis* polarizes to the right. Concentrated sulphuric acid converts all the different kinds of turpentine-oil into inactive turpentine, or *camphene.*

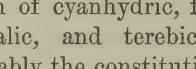
Turpentine-oil takes up oxygen from the air, and becomes thick and resinous. The oxygen absorbed shows all the properties of ozone. With strong oxidizing agents, as fuming nitric acid, the oil ignites.

On standing some time with water, it takes up two mole-

cules, and changes into a crystalline substance, *terpin*, $C_{10}H_{20}O_2$, which crystallizes with one molecule of water, becomes anhydrous at 100°, fuses at 103°, and sublimes in needles.

By leading chlorhydric acid gas into an alcoholic solution of turpentine-oil, they unite, the latter taking up two molecules of HCl, and forming the compound $C_{10}H_{17}Cl_2$, *terpene dihydrochloride*. When the chlorhydric acid is passed into dry turpentine-oil, the compound $C_{10}H_{17}Cl$, *terpene monohydrochloride*, is produced. This is isomeric with borneol chloride, and exists in a liquid and a solid modification.

On boiling with dilute nitric acid, it is vitally decomposed, with the formation of cyanhydric, formic, acetic, propionic, butyric, terephthalic, and terebic acids. *Terebic Acid*, $C_7H_{10}O$, has probably the constitution :



Terpene Dibromide, $C_{10}H_{16}Br_2$, which is formed by the action of bromine, loses 2 HBr on heating, yielding cymene (methylpropylbenzene). The production of terephthalic acid and cymene proves that terpene contains the benzene nucleus.

By repeated distillations, as well as by treatment with various acids, turpentine-oil is converted into the inactive camphene, $C_{10}H_{16}$, which is a crystalline mass, fusing at 58° and boiling at 160°.

Lemon-oil, $C_{10}H_{16}$, is obtained by pressing lemon-skins. It is lighter than water, boils at 175°, and has the odor of lemons. It unites with 2 HCl.

Among the oils containing oxygen we shall mention

Valerian-oil, which is obtained from the roots of the valerian. It is a mixture of valerianic acid, $C_5H_{10}O_2$, valerene, $C_{10}H_{16}$, and valerianic esters; its components can be separated by fractional distillation.

Caraway-oil, is contained in the seeds of the *Carum carui*. It contains a hydrocarbon, $C_{10}H_{16}$, and *carvol*, $C_{10}H_{14}O$.

Roman caraway-oil is produced from the *Cuminum cyminium*. It is mixture of cymene, $C_{10}H_{14}$, with cumic aldehyde, $C_{10}H_{14}O$.

Clove-oil is obtained from cloves by distillation with steam. It is a

mixture of a solid hydrocarbon, $C_{20}H_{32}$, which boils at 254°, with *eugenol*, $C_{10}H_{12}O_2$. Eugenol is an oily liquid boiling at 247°, which by fusion with potassium hydroxide is decomposed into protocatechuic and acetic acids. Its constitution is, $C_6H_3\begin{cases}OH\\OCH_3\\C_3H_5\end{cases}$. Eugenol is the monomethyl ether of allylpyrocatechol, and stands in intimate relation to *coniferyl alcohol*, $C_6H_3\begin{cases}OH\\OCH_3\\C_3H_4{-}OH\end{cases}$ (compare glucosides), and to *ferulic acid*,

$$C_6H_3\begin{cases}OH\\OCH_3\\C_3H_2CO_2H\end{cases},$$

which exists in asafœtida.

Thyme-oil, from *Thymus vulgaris*, consists of a hydrocarbon, $C_{10}H_{16}$, *thymene*, and *thymol*, the phenol of α-cymene.

Parsley-oil, contains a hydrocarbon, $C_{10}H_{16}$, and the so-called parsley-camphor, $C_{12}H_{14}O$.

Wormwood-oil, from *Artemesia absynthium*, is a dark-green oil, which contains a hydrocarbon, $C_{10}H_{16}$, a body isomeric with camphor, $C_{10}H_{16}O$, and a blue hydrocarbon, probably $C_{20}H_{42}$, boiling at about 290°.

Rose oil is a mixture of solid hydrocarbons, $C_{16}H_{34}$, with an oxygenated substance which has not been fully examined.

Anise-oil and *Fennel-oil* contain *anethol*, $C_{10}H_{12}O$, as their chief constituent. It fuses at 21° and boils at 232°, and by oxidation is converted into anise-aldehyde and anisic acid. Its constitution is $C_6H_4\begin{cases}OCH_3\\C_3H_5\end{cases}$.

Bitter Almond-oil contains benzaldehyde, $C_6H_5{-}CHO$, and cyanhydric acid. *Cinnamon-oil*, consists of cinnamic aldehyde, $C_6H_5{-}CH{=}CH{-}CHO$.

We have already met with a representative of the sulphuretted oils in mustard oil, C_3H_5NCS, and leek-oil (allyl sulphide) $(C_3H_5)S_2$. *Spoon-wort-oil* is the mustard-oil of the secondary butyl alcohol, C_4H_9NCS.

Resins.

The resins are obtained, together with the essential oils, from plants. They are either dissolved in the essential oils, in which case they are called *balsams*, or are mixed with gum, being then known as *resins*. As the essential oils take up

oxygen on standing, becoming more consistent, the balsams on exposure gradually become hard.

The resins are mostly amorphous, brittle bodies, which are insoluble in water and soluble in alcohol, ether, fatty, and essential oils. They are fusible, but decompose at a higher temperature. They exhibit acid properties.

Turpentine contains, besides turpentine-oil, a resin called *colophony, rosin,* or ordinary *resin,* which consists chiefly of *sylvic acid,* $C_{44}H_{64}O_5$, and an isomeric amorphous acid, *pinic acid. Copaiba balsam* contains copaiba-resin, which consists chiefly of *copaibic acid,* $C_{20}H_{30}O_2$. It forms transparent, colorless crystals. *Guaiacum resin,* from *guaiacum officinalis,* forms reddish-brown spherical masses which, when exposed to the air, or treated with chlorhydric acid, are colored green. Its alcoholic solution is colored dark-blue by nitrous acid and ozone. *Shellac* is easily soluble in alcohol and alkalis, and is used in the preparation of varnishes and sealing-wax. *Balsam* of *Peru* contains, besides the resin, cinnamic acid, cinnameïn (cinnamic benzyl ester, p. 272), and styracin (cinnamic cinnyl ester, p. 272). *Storax* contains, besides a resin, styracin as chief constituent, and also cinnamic acid and styrene, C_8H_8. *Balsam of Tolu* contains various resins, benzoic acid, and an essential oil boiling at 170°. *Benzoin resin,* serves as the source of benzoic acid, containing 18 % of it. *Aloes,* from *Aloe capensis* is a deep brown, or when made from *Aloe succotrina,* a reddish-brown amorphous mass, which on treatment with water yields aloïn (see later). *Jalap* is a yellowish-brown mass. *Mastic* forms bright-yellow grains with a balsamic odor and taste.

Gum Ammoniac is the dried milky sap of the *Dorema ammoniacum,* and forms yellow to yellowish-brown grains, which on fusion with potassium hydroxide yield, besides volatile fat acids and oxalic acid, resorcinol. *Gum galbanum* is the dried milky sap of the *Ferula erubescens. Asafœtida* is the dried milky sap of the *Scorodosma fœtidum,* and is an offensively

smelling brownish resin, which owes its odor to a sulphuretted oil, $C_{12}H_{22}S_2$, boiling at 135°. On fusion with potassium hydroxide, it yields, besides volatile fatty acids, protocatechuic acid and resorcinol. *Euphorbium* is obtained from *Euphorbia resinifera*. Its active constituent is *euphorbon*, which is the anhydride of an acid not yet thoroughly examined. Among the remaining gums are *gum-elimi*, *frankincense*, and *myrrh*.

Caoutchouc is intimately related to the resins. Many trees, especially those of the *euphorbiaceæ*, yield a juice, when incisions are made in them, that gradually hardens in the air to an elastic mass. Its composition corresponds to the formula C_8H_{14}. When caoutchouc is heated with sulphur, it becomes "vulcanized," and is then much more elastic and does not become brittle when cold. On heating higher, it is converted into a peculiar substance known as "vulcanite," or hard rubber.

A substance very similar to caoutchouc occurs in the East Indies, which is known as *gutta percha*, and has the composition $C_{10}H_{16}$. It is produced by a tree belonging to the sapodilla family, and is obtained in the same way as caoutchouc.

To conclude, we shall mention the fossil resins, amber and *asphalt*. The former is found on the coast of the Baltic Sea, contains a resin, amber oil, and succinic acid. The latter has probably been formed from petroleum, and is a black mass fusing about 100°.

Pyridine Bases.

There are several nitrogeneous substances which have the same composition as aniline and its homologues, but which are different from them. They do not contain the benzene nucleus, and the lowest member of the series has less than six carbon atoms. They occur in coal-tar and in animal oil (Dip-

pel's oil), and are formed by the decomposition of the alkaloids. Some of them have been produced artifically. The nitrogen in them is bound to the carbon by three bonds, so that they may be considered as nitrile-bases, while aniline and its homologues are amido-bases. At present there are known

Pyridine,	C_5H_5N		
Picoline,	C_6H_7N	Methylpyridine,	(isomeric with aniline)
Lutidine,	C_7H_9N	Dimethypyridine,	(isomeric with toluidine)
Collidine,	$C_8H_{11}N$	Trimethylpyridine,	(isomeric with xylidine)
Parvoline,	$C_9H_{13}N$	Tetramethylpyridine,	(isomeric with cumidine)

Picoline and collidine have been produced artificially.

Picoline is formed by heating the compound of acroleïn-ammonia, $2\,C_3H_4O\,.\,NH_3$:

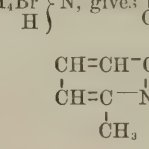
$$C_6H_5O_2\,.\,NH_3 = C_6H_7N + 2\,H_2O.$$

Picoline is also obtained by heating allyl tribromide, $C_3H_5Br_3$, with ammonia:

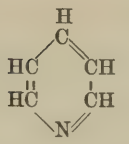
$$2\,C_3H_5Br_3 + NH_3 = C_6H_7N + 6\,HBr.$$

The reaction takes place in two steps. At first, *dibromallylamine,* $\left.\begin{matrix}C_3H_4Br\\C_3H_4Br\\H\end{matrix}\right\}N$, is formed, which then yields picoline by the elimination of 2 HBr. We can therefore easily understand the constitution of picoline.

$$\left.\begin{matrix}C_3H_4Br\\C_3H_4Br\\H\end{matrix}\right\}N, \text{ gives } \begin{matrix}C_3H_4\\|\\C_3H_4\end{matrix}\!\!>N, \text{ or}$$



Pyridine is, hence, constituted analogously to benzene



i.e. it is a benzene-ring in which a CH-group is replaced by an N. The other bases of this series are homologues of pyridine, picoline being methylpyridine, etc.

Ethylidene chloride and ammonia yield collidine :

$$4\,CH_3{-}CHCl_2 + NH_3 = C_8H_{16}N + 8\,HCl.$$

All of these substances are liquid, and have a peculiar and penetrating odor and a bitter taste. They are volatile without decomposition, and possess basic properties, *i.e.* they unite like ammonia directly with acids to form salts. The lower members are miscible with water, the higher ones are soluble in it. The isomeric relations which exist in the benzene derivatives, also appear in the pyridine derivatives. From the formula of pyridine we see that there are three methylpyridines (picolines) possible (they are all three known). The number of isomers in the higher homologues is, of course, greater.

The pyridine bases have lately acquired a greater interest, as they have been found to constitute the basis of the more important alkaloids. By oxidation of pyridine as well as of the alkaloids, pyridine-carboxylic acids,

$$C_5H_4N{-}CO_2H,\quad C_5H_3N(CO_2H)_2,\ \text{etc.},$$

are formed.

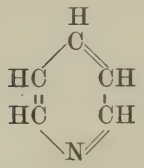
There are a number of other bases found in coal-tar, which are related to the pyridine bases, viz. :

Quinoline, C_9H_7N
Lepidine, $C_{10}H_9N$
Cryptidine, $C_{11}H_{11}N$.

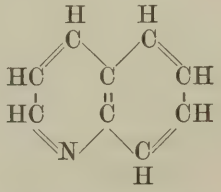
They are obtained by the decomposition of quinine, strych-

nine, etc. Quinoline stands to pyridine in the same relation as naphthalene to benzene :

Pyridine :



Quinoline :



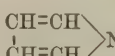
We see from the above figure that in the quinoline bases the nitrogen has no replaceable hydrogen. They are oils insoluble in water.

Quinoline is produced synthetically when nitrobenzene or aniline is heated with glycerol and sulphuric acid :

$$C_6H_5NO_2 + C_3H_8O_3 = C_9H_7N + H_2O + O_2$$
$$C_6H_5NH_2 + C_3H_8O_3 = C_9H_7N + H_2O + H_2.$$

A similar constitution may be ascribed to another class of bodies whose chief representative is *pyrrole*, C_4H_5N, which is obtained by the dry distillation of nitrogenous substances (coal, bones, etc.). Pyrrole is a colorless liquid with an odor like chloroform. It is insoluble in water and soluble in acids. It is, however, not properly a base, for it can be entirely removed from its solution in an acid by boiling. It colors a splinter of pine, moistened with chlorhydric acid, purplish-red, and may be thus detected. Pyrrole acquires easily a brown color, and an amorphous red substance separates, which is called *pyrrole-red*, $C_{12}H_{14}N_3O$,

The constitution of pyrrole is probably

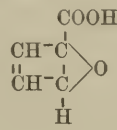


It is also formed by the distillation of ammonium mucate :

$$C_6H_9O_8{}^-NH_4 = C_4H_5N + 2\ CO_2 + 4\ H_2O.$$

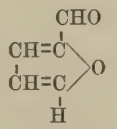
By the distillation of mucic acid by itself, *pyromucic acid*, $C_5H_4O_3$, is

obtained. This acid is also formed by boiling furfurole with moist silver oxide. It is a monobasic acid. Its ammonium salt yields pyrrole on heating. Its constitution is perhaps :



On distilling pyromucic acid with an excess of soda-lime, carbonic acid splits off, and *tetrol*, or *tetraphenol*, C_4H_4O, is obtained. It is a colorless liquid boiling at 32°, and has a peculiar odor.

The aldehyde of pyromucic acid is known under the name *furfurole*. C_5H_4O. It is obtained by the distillation of clover, meal, sawdust, etc. with dilute sulphuric acid. It unites with the acid sulphites of the alkalis, and, on boiling with silver oxide, is converted into pyromucic acid. Its constitution is hence :



Alkaloids.

We now come to a large class of very important nitrogenous substances which occur in many plants, and which, on account of their energetic action on the organism, have numerous uses. They all possess basic properties, and are hence called in a limited sense, *organic bases*, or *alkaloids*. Their constitution is in most cases not yet understood, but the majority of them seem to be derivatives of the pyridine bases.

The alkaloids are all practically insoluble in water, but give soluble salts with acids. They are set free from the solutions of their salts by alkalis and alkaline carbonates, being precipitated as free alkaloids. Tartaric acid hinders the precipitation of the alkaloids with the exception of strychnine, narco-

tine and cinchonine. They are all soluble in alcohol, but not all in ether. They are precipitated from solutions of their salts by tannic acid, potassium mercuric iodide, potassium cadmium iodide, phosphomolybdic acid, phosphotungstic acid, and metatungstic acid.

They are obtained by extracting the pulverized plants with acidified water, and when the alkaloid is volatile, distilling, after the addition of an alkali. If the base is not volatile, which is generally the case, the base is precipitated with an alkali. The precipitated alkaloid is purified by again dissolving in an acid, recrystallizing the salt, and reprecipitation by an alkali.

Some alkaloids contain only carbon, hydrogen, and nitrogen, while others also contain oxygen. The former are liquid at ordinary temperatures, the others mostly solid and crystalline.

Conine, $C_8H_{15}N$, exists already formed in the hemlock (*Conium maculatum*), and is obtained from the seeds by distillation with water. It is a colorless liquid with a stupefying odor, boiling at 168°. It possesses extremely poisonous properties. It dissolves in 100 parts of water, and in the cold dissolves some water, but not when warm. Moist conine for this reason becomes turbid when warmed, even the warmth of the hand affecting it. Its aqueous solution reacts strongly alkaline, and completely neutralizes strong acids. It becomes brown and thick when exposed to the light, decomposing with evolution of ammonia. Oxidizing agents convert it into butyric acid, $C_4H_8O_2$. It coagulates a solution of albumin. Dry chlorhydric acid gas colors it at first purplish-red and then deep blue.

It absorbs nitrous acid gas. Conine saturated with nitrous acid gas, when treated with water, yields *azoconhydrine*, $C_8H_{16}N_2O$, which separates as a bright-yellow oil, and by the action of phosphoric anhydride is converted into water, nitrogen, and *conylene*, C_8H_{14}.

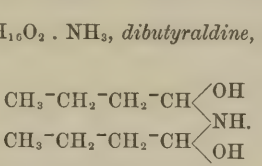
Conine has not yet been produced artificially, but a com-

pound isomeric with it and resembling it very much, *paraconine*, is obtained by the action of ammonia on butylaldehyde.

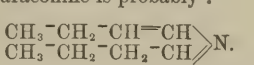
Normal butyl aldehyde unites with two molecules of ammonia, forming $C_4H_8O \cdot NH_3$ and $C_8H_{16}O_2 \cdot NH_3$. The latter yields on dry distillation paraconine, water being eliminated :

$$C_8H_{16}O_2 \cdot NH_3 = C_8H_{15}N + 2\,H_2O.$$

The compound, $C_8H_{16}O_2 \cdot NH_3$, *dibutyraldine*, possesses the constitution :



The constitution of paraconine is probably :



Conine is an amido-base. The H of the NH-group can be replaced by hydrocarbon rests (CH_3, C_2H_5, etc.) and the resulting bases unite with acids, forming salts, and with chlorides, bromides, etc., producing ammonium compounds.

Standing between conine and dibutyraldine, is *conhydrine*, $C_8H_{17}NO$, which is also contained in the seeds of the hemlock. It crystallizes in mother-of-pearl leaflets fusing at 121° and boiling at 240°. It possesses weak basic properties.

Nicotine, $C_{10}H_{14}N_2$. This base is found in the leaves of the tobacco, and is obtained from them by extraction with dilute sulphuric acid. The different kinds of tobacco contain varying amounts of nicotine, ordinary tobacco containing from 7–8%, while the finest Havana tobacco contains less than 2%. Nicotine is a colorless liquid with a penetrating odor of tobacco and a burning taste. It boils at 250° with partial decomposition. It is easily soluble in water, alcohol, and ether. On exposure to the air it turns brown. It is very poisonous. It is a di-valent tertiary base, its nitrogen containing, therefore, no substitutable hydrogen.

On oxidation it is converted into *nicotinic acid* (pyridin-carboxylic acid), $C_6H_5NO_2 = C_5H_4N{\cdot}COOH$. This acid fuses at 224°, and crystallizes in needles. Its constitution is unknown.

Sparteïne, $C_{15}H_{26}N_2$, occurs in *Spartium scoparium.* It is a thick, colorless oil with a bitter taste, and boils at 288°. It is a di-valent tertiary base.

The constitutions of the alkaloids containing oxygen are very complicated, and have been still less investigated than the preceding. In a few, it has been proved that the oxygen exists in the form of hydroxyl or CO.

Opium Bases. By making incisions in the green seed-capsules of the poppy (*Papaver somniferum*) a white, milky sap is obtained, which, when dried, constitutes opium. Opium contains a large number of alkaloids, of which we can consider but a few of the more prominent. The most important alkaloid in opium is *morphine,* and the value of the opium is estimated by the amount of this base that it contains.

Opium bases :	Morphine	$C_{17}H_{19}NO_3$	
	Codeïne	$C_{18}H_{21}NO_3$	
	Codamine	$C_{20}H_{23}NO_4$	
	Laudanine	$C_{20}H_{25}NO_4$	
	Pseudomorphine	$C_{17}H_{19}NO_4$	
	Thebaïne	$C_{19}H_{21}NO_3$	isomeric
	Thebenine	$C_{19}H_{21}NO_3$	isomeric
	Protopine	$C_{20}H_{19}NO_5$	
	Papaverine	$C_{21}H_{21}NO_4$	
	Deuteropine	$C_{20}H_{21}NO_5$	
	Cryptopine	$C_{21}H_{23}NO_5$	
	Meconidine	$C_{21}H_{25}NO_4$	
	Laudanosine	$C_{21}H_{27}NO_4$	
	Rhoeadine	$C_{21}H_{21}NO_6$	isomeric
	Rhoeagenine	$C_{21}H_{21}NO_6$	isomeric
	Narcotine	$C_{22}H_{23}NO_7$	
	Narceïne	$C_{23}H_{29}NO_9$	[rine ?)
	Lanthopine	$C_{23}H_{25}NO_4$	(homologous with papave-

Morphine, $C_{17}H_{19}NO_3$. On boiling opium with water, the

morphine goes into solution in combination with certain acids (particularly meconic acid). From this solution, it is precipitated, after neutralizing a part of the acids with milk of lime, by ammonium chloride.

Morphine is precipitated by a solution of lime, but is redissolved by an excess. It behaves in the same manner with alkalis. In ammonia, however it is insoluble.

In cold water and ether it is almost insoluble. It dissolves in 500 parts of boiling water and in 40 parts of alcohol. It crystallizes in glittering, colorless, rhombic crystals containing a molecule of water, which it loses on fusion. On stronger heating, it carbonizes.

A solution of morphine turns the ray of polarized light to the left.

It is a strong base, and its salts are soluble in alcohol and water. The *hydrochloride*, $C_{17}H_{19}NO_3 . HCl + 3\,H_2O$, *acetate*, $C_{17}H_{19}NO_3C_2 . H_4O_2 + H_2O$, and *sulphate*,

$$(C_{17}H_{19}NO_3)_2 . H_2SO_4 + 5\,H_2O,$$

are worthy of mention. They all crystallize in fine needles.

Morphine salts, when treated with nitric acid, turn first red and then yellow. Ferric chloride colors them deep blue. A solution of morphine in a little concentrated sulphuric acid is colored violet on the addition of sulphuric acid containing nitric acid.

The nitrogen in morphine does not bind any substitutable hydrogen. It is hence a nitrile base.

By heating morphine a considerable time with fuming chlorhydric acid, it is converted into *apomorphine*, $C_{17}H_{17}NO_2$. Apomorphine is a white powder which, on exposure to the air, becomes quickly colored green. It is a powerful emetic.

Codeïne, $C_{18}H_{21}NO_3$, is homologous with morphine. It crystallizes with one molecule of water, is somewhat soluble in

water, and fuses at 150°. At a higher temperature it is decomposed. Chlorine, bromine, and iodine yield substitution products. It is also a nitrile base.

Narcotine, $C_{22}H_{23}NO_7$, crystallizes in rhombic prisms fusing at 176°. It is almost insoluble in water, easily soluble in alcohol and ether. It is a weak base, its salts being decomposed by boiling with water.

On heating with chlor-, or iodohydric acid, narcotine loses successively three methyl-groups. On heating with water, it breaks into *cotarnine*, $C_{12}H_{13}NO_3$, and *meconine*, $C_{10}H_{10}O_4$, and by heating with dilute nitric acid, into cotarnine, *opianic acid*, $C_{10}H_{10}O_5$, and *hemipinic acid*, $C_{10}H_{10}O_6$:

$$C_{22}H_{23}NO_7 = C_{12}H_{13}NO_3 + C_{10}H_{10}O_4,$$
$$C_{22}H_{23}NO_7 + O = C_{12}H_{13}NO_3 + C_{10}H_{10}O_5, \text{ etc.}$$

Hemipinic acid is decomposed by iodohydric acid into methyl iodide, carbonic acid, and protocatechuic acid, $C_7H_6O_4$:

$$C_{10}H_{10}O_6 + 2\,HI = 2\,CH_3I + CO_2 + C_7H_6O_4.$$

The constitution of hemipinic acid is, $C_6H_2(CO_2H)_2(OCH_3)_2$. Opianic acid is the aldehyde of hemipinic acid, $C_6H_2(OCH_3)_2\langle\begin{matrix}COOH\\CHO\end{matrix}$, and meconine is the internal anhydride of the alcohol derived from opianic acid, $C_6H_2(OCH_3)_2\langle\begin{matrix}CO\\CH_2\end{matrix}\rangle O$.

The opium-bases are chiefly combined in opium with a peculiar acid called *meconic acid*, $C_7H_4O_7$, which crystallizes with $3\,H_2O$ in colorless, rhombic tablets difficultly soluble in cold water, more easily in hot, easily in alcohol. It is characterized by giving a deep red solution with ferric chloride. On continued boiling with hot water, or dilute chlorhydric acid, it breaks into carbonic acid and *comenic acid*, $C_6H_4O_5$. The latter forms hard, difficultly soluble grains, and by distillation falls into carbonic acid and *pyromeconic acid*, $C_5H_4O_3$.

Cinchona Bases. The following important alkaloids are found in the bark of the cinchona tree :

$$\left.\begin{matrix}\text{Quinine}\\ \text{Quinidine}\end{matrix}\right\} C_{20}H_{24}N_2O_2,$$

$$\left.\begin{matrix}\text{Cinchonine}\\ \text{Cinchonidine}\end{matrix}\right\} C_{19}H_{22}N_2O.$$

Quinine and quinidine are distinguished from the other two by their greater solubility in ether, and also by giving with chlorine water and ammonia a green solution. The most important of them is quinine.

Quinine, $C_{20}H_{24}N_2O_2$, is extracted from the cinchona bark by dilute sulphuric acid. The acid solution is precipitated with sodium carbonate and purified by crystallizing from alcohol or ether. It crystallizes with 3 H_2O in silky needles. It is difficultly soluble in water. With acids, it gives two series of salts. The hydrochloride and sulphate are used medicinally.

Quinine Hydrochloride, $C_{20}H_{24}N_2O_2 . HCl + 2\ H_2O$, forms white, silky needles soluble in 20 parts of water.

Quinine Sulphate, $(C_{20}H_{24}N_2O_2)_2 . H_2SO_4 + 8\ H_2O$, crystallizes in large glittering needles which effloresce in the air, and gradually fall to a white powder, losing 6 molecules of water of crystallization. It is soluble in 800 parts of cold water, but easily in hot water and alcohol.

Quinine Acid Sulphate, $C_{20}H_{24}N_2O_2 . H_2SO_4 + 7\ H_2O$, crystallizes in glittering needles, efflorescing in the air. They are soluble in 10 parts of water, and the aqueous solution possesses a strong blue fluorescence.

Quinine Valerianate, $C_{20}H_{24}N_2O_2 . C_5H_{10}O_2 + H_2O$, is formed by the neutralization of an alcoholic quinine solution, with valerianic acid. Colorless crystals with a bitter taste and the odor of valerianic acid.

Quinine Tannate, is a yellow amorphous precipitate produced by adding a solution of tannic acid to solutions of quinine salts. It has a peculiar odor and a bitter astringent taste. It is almost insoluble in water and very difficultly in alcohol.

Quinine is a nitrile base. It polarizes to the left. When heated with potassa-lye it yields quinoline and its homologues,

which are isomeric, but not identical, with those obtained from coal-tar and Dippel's-oil.

By oxidation with potassium permanganate, *pyridin-tricarboxylic acid* is obtained, $C_8H_5NO_6 = C_5H_2N(CO_2H)_3$, which on heating breaks into carbonic acid and *pyridin-dicarboxylic acid*, $C_7H_5NO_4$, fusing at 254°.

Quinine is used in medicine as an antifebrile agent. The green color which it forms with ammonia and chlorine water is characteristic of it.

In most cinchona barks, there is found besides quinine, *Cinchonine*, $C_{19}H_{22}N_2O$, which has properties similar to those of quinine, although it is not so strong an antifebrile. It forms white, glittering, odorless prisms, with a bitter taste, which at first is hardly perceptible. It is difficultly soluble in water. On oxidation, it yields *cinchoninic acid* (*quinoline-carboxylic acid*), $C_8N_5HO_6$, and *pyridine-tricarboxylic acid*, $C_8N_5NO_6$. The following salt is worthy of mention :

Cinchonine Sulphate, $(C_{19}H_{22}N_2O)_2 \cdot H_2SO_4 + 2\,H_2O$, forms white glittering crystals, somewhat soluble in water.

Many quinine barks contain also quinidine and cinchonidine. *Quinidine*, $C_{20}H_{24}N_2O_2$, crystallizes with $2\,H_2O$, and polarizes to the right. It is also a nitrile base. *Cinchonidine*, $C_{19}H_{22}N_2O$, forms anhydrous crystals. It solutions polarize to the left. It is also used as an antifebrile.

Two alkaloids occur in the cusco chinchona-barks, viz., *Cusconine* and *Aricine*, both having the formula, $C_{23}H_{26}N_2O_4$.

The sulphate of the former is a characteristic salt, forming a gelatinous precipitate almost insoluble in water. The acid oxalate of aricine is also characteristic. It crystallizes in white prisms which after a short time change into rhombohedrons very difficultly soluble in water. Both alkaloids polarize to the left.

In the cinchona barks an acid, *quinic acid*, $C_7H_{12}O_6$, occurs, which is combined partly with the alkaloids and partly with calcium. It is monobasic, and hence contains only one carboxyl group, and belongs to the

aromatic series. It is derived from a completely reduced benzene molecule (C_6H_{12}), $C_6H_7(OH)_4COOH$. It forms colorless rhombic prisms easily soluble in water, and polarizing to the left. On oxidation it yields quinone, and on reduction benzoic acid. On fusion with potassium hydroxide, it affords protocatechuic acid, $C_7H_6O_4$.

The cinchona barks (and the tormentillo root) contain besides *chinovic acid*, $C_{24}H_{38}O_4$, a glucoside, *chinovin*, $C_{30}H_{48}O_8$, which is decomposed by acids into a sugar, $C_6H_{12}O_6$, and chinovic acid. In them is also found a peculiar tannic acid called, *quinotannic acid*, which gives a green precipitate with ferric salts, and is converted by the oxygen of the air into a red coloring matter, *cinchona-red*.

Strychnine and brucine are found in the seeds of the *Strychnos nux vomica*, the beans of the *St. Ignatius-bean*, (*Strychnos ignatii*) and in *snake-wood* (roots of the *Strychnos colubria*).

Strychnine, $C_{21}H_{22}N_2O_2$, is obtained by extracting the Barbadoes-nuts, or Ignatius-beans with boiling alcohol, and after throwing down the impurities with lead oxide, precipitating the strychnine and brucine with magnesia, and separating the strychnine by cold alcohol, in which the brucine is alone soluble. Strychnine crystallizes in colorless, rhombic columns which taste very bitter, are almost insoluble in water, absolute alcohol, and ether, but are easily soluble in ordinary alcohol.

It is colored violet-blue by potassium chromate and sulphuric acid. Nitric acid does not color it when free from brucine. It is a nitrile base, and unites with acids to form salts.

It is extremely poisonous, causing tetanus even in small doses. It is used in medicine.

Strychnine Nitrate, $C_{21}H_{22}N_2O_2 . HNO_3$, forms colorless, silky needles with an extremely bitter taste, but little soluble in water and cold alcohol, more easily in hot alcohol.

Brucine, $C_{23}H_{26}N_2O_4$, crystallizes with four molecules of water in four-sided prisms which effloresce when exposed to the air. It tastes very bitter, is difficultly soluble in water,

insoluble in ether, but easily in alcohol. Nitric acid colors it red, giving a solution from which stannous chloride precipitates a violet substance.

Its physiological action is less violent than that of strychnine. It is converted into strychnine by oxidation with dilute nitric acid :

$$C_{23}H_{26}N_2O_4 + 4\,O = C_{21}H_{22}N_2O_2 + 2\,CO_2 + 2\,H_2O.$$

Atropine, $C_{17}H_{23}NO_3$, is found in the berries of the deadly nightshade (*Atropa belladonna*) and in the thorn-apple (*Datura stramonium*). It crystallizes in thin needles which are easily soluble in alcohol, very difficultly in water and ether. It fuses at 115°, and is decomposed at a high temperature. It tastes intensely bitter, is very poisonous, and passes unchanged into the urine. It possesses the peculiar property of dilating the pupil very strongly, and is hence used in treatment of the eye. Its salts do not crystallize.

On boiling with strong bases or acids, it is decomposed into *tropine*, $C_8H_{15}NO$, and *tropic acid*, $C_9H_{10}O_3$:

$$C_{17}H_{23}NO_3 + H_2O = C_8H_{15}NO + C_9H_{10}O_3.$$

On the other hand, tropine and tropic acid, when heated for a considerable time with very dilute chlorhydric acid at 100°, are converted into atropine.

Atropine sulphate, $(C_{17}H_{23}NO_3)_2 . H_2SO_4$, is a white, bitter powder, very easily soluble in water and alcohol.

Hyoscyamine, $C_{17}H_{23}NO_3$, is the active principle of henbane (*Hyoscyamus niger*). It crystallizes in soft, silky needles soluble in alcohol, water, and ether. It fuses at 90°, and dilates the pupils. It possesses a sharp, offensive taste. When pure, it is odorless, but when impure has a strong offensive and stupefying odor.

On boiling with acids or strong bases, it breaks into tropine, $C_8H_{15}NO$,

and tropic acid, $C_9H_{10}O_3$, yielding the same decomposition-products as atropine.

Aconitine, $C_{30}H_{47}NO_7$, exists in the purple monk's-hood (*Aconitum napellus*) and forms a colorless powder without odor and with a bitter taste, causing a roughness in the throat. It is difficultly soluble in water, easily in alcohol.

Veratrine, $C_{32}H_{49}NO_9$(?), is found in the seeds of the sabadilla (*Veratrum sabadilla*) and, with *jervine,* in the roots of the white hellebore (*Veratrum album*). It is extracted with dilute chlorhydric acid. It crystallizes in rhombic prisms which effloresce in the air, fuse at 205°, are insoluble in water and easily soluble in alcohol and ether. It is very poisonous; the smallest amount brought in the nose, causes the most violent sneezing. Concentrated sulphuric acid colors it first yellow and then carmine-red. With concentrated nitric acid, it yields a dark violet solution on the surface of which drops of oil are formed. It forms crystalline salts.

Jervine, $C_{30}H_{46}N_2O_3 + 2\,H_2O$, is found, together with veratrine, in the roots of the white hellebore. It forms colorless prisms insoluble in water. With acids, it forms salts, most of which are very difficultly crystallizable.

Berberine, $C_{20}H_{17}NO_4$, exists in the roots of the *Berberis vulgaris.* It crystallizes with five molecules of water in fine yellow needles which lose their hydrate-water at 100°, fuse at 120° and decompose at a higher temperature. It is insoluble in water. Nascent hydrogen converts it into *hydroberberine,* $C_{20}H_{21}NO_4$.

Piperine, $C_{17}H_{19}NO_3$, is extracted from pepper by boiling with alcohol. Alkalis decompose it into *piperinic acid,* $C_{12}H_{10}O_4$, and *piperidine,* $C_5H_{11}N$.

$$C_{17}H_{19}NO_3 + H_2O = C_{12}H_{10}O_4 + C_5H_{11}N.$$

Piperine forms colorless columns fusing at 100°, insoluble in water, easily soluble in alcohol and ether. *Piperinic acid,*

$C_{12}H_{10}O_4$, a bright-yellow, crystalline substance insoluble in water, yielding protocatechuic acid, $C_7H_6O_4$, on fusion with potassium hydroxide. *Piperidine*, $C_5H_{11}N$, is a colorless, strongly alkaline liquid boiling at 106°, and forming well crystallizing salts. The nitrogen of piperidine binds a substitutable atom of hydrogen, showing it to be an imido-base. *Methylpiperidine*, $C_5H_{10}N{-}CH_3$, *ethylpiperidine*, *benzoylpiperidine*, etc., have also been obtained. On heating with bromine, *dibromoxypyridine*, $C_5H_3NBr_2O$, is formed.

The constitution of piperine is

$$C_5H_{10}{-}N{-}CO{-}C_4H_4{-}C_6H_3\begin{matrix}O\\O\end{matrix}CH_2,$$

and of piperidine

$$CH_2\begin{matrix}CH_2{-}CH_2\\CH_2{-}CH_2\end{matrix}NH.$$

It is hence hexahydropyridin.

Besides the alkaloids which have been mentioned above, there is a great number of others, of which we shall only mention the following.

Eserine, or *physostigmine*, $C_{15}H_{21}N_3O_2$, occurs in the Calabar-bean, and is an intensely poisonous substance. It causes a contraction of the pupils. It is easily soluble in alcohol and ether, its solution decomposing very easily when exposed to the air.

Sinapine, $C_{16}H_{23}NO_5$, exists as sulphocyanate in the seeds of the white mustard. The free base, owing to its instability, has not been obtained. The sulphocyanate forms fine needles fusing at 130°. On boiling with an alkali, it is decomposed into *neurine*, $C_5H_{15}NO_2$, and *sinapic acid*, $C_{11}H_{12}O_5$.

Lycine, $C_5H_{11}NO_2$, is found in the leaves of *Lycium barbarum*.

Curarine, $C_{10}H_{15}N$, exists in curare, the Indian arrow poison.

Harmaline, $C_{13}H_{14}N_2O$ } in the seeds of *Peganum harmala*.
Harmine, $C_{13}H_{12}N_2O$ }

Cocaïne, $C_{17}H_{21}NO_4$, in the leaves of the cocoa.

Colchicine, $C_{17}H_{19}NO_5$, is obtained from the seeds of the *Colchicum autumnale*, and is an amorphous powder which acts as a powerful emetic.

Corydaline, $C_{18}H_{19}NO_4$, is contained in the seeds of the *Bulbocapnus cavus*.

Chelidonine, $C_{19}H_{17}NO_4$, is extracted from the roots of the *Chelidonium majus*.

Emetine, $C_{30}H_{46}N_2O_7$, exists in the ipecacuanha root (*Radix ipecacuanha*). It is a white, easily decomposable powder, fusing at 70°. It is a strong emetic.

Solanine, $C_{43}H_{71}NO_{16}$, is contained in the germs of the potato. It forms colorless needles with a bitter taste, difficultly soluble in water, and fusing at 235°. By boiling with dilute acids, it splits into sugar and *solanidine*, $C_{25}H_{41}NO$, which forms fine, silky needles, fusing at over 200°. It yields difficultly soluble, finely crystallizable salts.

Glucosides.

It has already been stated (p. 163) that the glucosides are substances occurring in plants, and are compounds of a sugar (usually dextrose) with other bodies, and are decomposed by the action of ferments, acids, and alkalis into their constituents. Since plants generally contain these ferments, this decomposition of the glucosides takes place when the plants are allowed to remain for a length of time in contact with water. We have already met with a number of glucosides, *e.g.* indican, which is a compound of indigo with dextrose, ruberythic acid, a compound of dextrose with alizarine, franguline, etc.

Amygdalin, $C_{20}H_{27}NO_{11}$, occurs in the bitter almonds, the leaves of the laurel, and the kernels of cherries, apricots, peaches, etc. It is obtained from bitter almonds (previously freed from fat), by boiling with alcohol. It forms small, glittering scales, which are odorless, and possess a weak, bitter

taste. It is converted by dilute acids, or by the ferment, *Emulsin*, which is contained in the almond, into dextrose, cyanhydric acid, and benzaldehyde :

$$C_{20}H_{27}NO_{11} + 2\,H_2O = 2\,C_6H_{12}O_6 + HCN + C_7H_6O.$$

On boiling with alkalis, it evolves ammonia and is decomposed into *amygdalic acid*, $C_{20}H_{28}O_{13}$, the CN-group being converted into COOH.

Salicin, $C_{13}H_{18}O_7$, occurs in the bark of the willow and of numerous poplars. It forms small, glittering, bitter prisms, fusing at 198°, and difficultly soluble in cold water, but easily in hot. Ferments, *e.g.* emulsin, decompose it into dextrose and salicylic alcohol (saligenin). By the action of dilute acids, it breaks into dextrose and *saleritin*, a resinous substance arising from the decomposition of saligenin :

$$C_{13}H_{18}O_7 + H_2O = C_6H_{12}O_6 + C_7H_8O_2.$$

Coniferin, $C_{16}H_{22}O_8 + 2\,H_2O$, exists in the cambial sap of the *coniferæ*, and separates on concentration to $\frac{1}{5}$ of its volume. It forms glittering, efflorescent needles, fusing at 185°, and difficultly soluble in cold water, more easily in hot water and alcohol. It is decomposed by ferments into sugar and coniferyl alcohol, $C_{10}H_{12}O_3$, and by oxidation into *sucrovanillic acid*, $C_{14}H_8O_9 + H_2O$, just as coniferyl alcohol is oxidized into vanillin, $C_8H_8O_3$, and vanillic acid, $C_8H_8O_4$ (methylprotocatechuic aldehyde and methylprotocatechuic acid).

Æsculin, $C_{15}H_{16}O_9 + 2\,H_2O$, occurs in the horse-chestnut, and forms fine, slightly bitter prisms, difficultly soluble in cold water and alcohol. Its solutions possess a blue fluorescence. It is decomposed by dilute acids into sugar and æsculetin, $C_9H_6O_4$. *Æsculetin*, $C_9H_6O_4 + H_2O$, forms colorless needles, very difficultly soluble in water and alcohol. On boiling with potassa-lye, it is decomposed into oxalic, formic, and protocatechuic acids.

Daphnin, which occurs in the barks of various species of daphnia, has the same composition as æsculin. With ferments and dilute acids, it yields *daphnetin*, an isomer of æsculetin.

Phloridzin, $C_{21}H_{24}O_{10} + 2\,H_2O$, exists in the bark of the roots of the apple, pear, cherry, and plum trees. It forms fine, white, silky, glittering, bitter prisms, which are easily soluble in hot water and alcohol. On decomposition, it yields besides sugar, *phloretin*, $C_{15}H_{14}O_5$, which crystallizes in small leaflets, and is decomposed by alkalis into *phloroglucin*, $C_6H_6O_3$, and *phloretic acid*, $C_9H_{10}O_3$.

Quercitrin, $C_{36}H_{38}O_{20}$, occurs in the bark of the *Quercus tinctoria*, and is a yellow powder difficultly soluble in water. With acids, it yields isodulcite and *quercetin*, $C_{24}H_{16}O_{11}$. The latter exists in tea and in the bark of the apple-tree and other plants. It is a yellow powder subliming in yellow needles. It is but little soluble in water, easily in alcohol. By fusing with potassium hydroxide, it is decomposed into phloroglucin and *quercetinic acid*, $C_{18}H_{12}O_9$, which crystallizes in small prisms, and is converted into several other acids by continued action of potassium hydroxide.

Hesperidin, $C_{22}H_{26}O_{12}$, exists in unripe oranges. It forms fine needles fusing at 245°. Acids break it into sugar and *hesperitin*, $C_{16}H_{14}O_6$, which fuses at 223°, and is decomposed by potassa-lye into phloroglucin and *hesperetinic acid*, $C_{10}H_{10}O_4$.

Arbutin, $C_{25}H_{34}O_{14}$, exists in the leaves of the arbutus. It crystallizes in needles fusing at 170°. It is decomposed by emulsin into sugar, quinol, and methylquinol.

Myronic acid, $C_{10}H_{19}NS_2O_{10}$, exists as a potassium salt in the seeds of the black mustard. It forms small, silky, glittering needles. It is decomposed by *myrosin*, a ferment existing in the seeds of the mustard, into sugar, mustard-oil, and potassium hydrogen sulphate :

$$C_{10}H_{18}KNS_2O_{10} = C_6H_{12}O_6 + C_3H_5{}^{-}NCS + KHSO_4.$$

Convolvulin, $C_{31}H_{50}O_{16}$, is found in jalap-root. It is an amorphous mass fusing at 150°. Ferments convert it into sugar and *convolvulinol*, $C_{13}H_{24}O_3 + \frac{1}{2}H_2O$. *Jalapin*, $C_{34}H_{56}O_{16}$, is found with convolvulin in the same root. It breaks into sugar and *jalapinol*, $C_{16}H_{30}O_3 + \frac{1}{2}H_2O$.

Saponin, $C_{32}H_{54}O_{18}$, occurs in numerous plants, particularly the soap-root. It is a white powder, the dust of which causes the most violent sneezing. Its solution foams like a soap solution, even when greatly diluted. It breaks into sugar and *Sapogenin*, $C_{14}H_{22}O_2$.

Helleborin, $C_{36}H_{42}O_6$, exists in *Helleborus viridis*, and *helleborein*, $C_{26}H_{44}O_{15}$, in *Helleborus niger*. They both crystallize in needles, and act as narcotics. The former decomposes into sugar and *Helleboresin*, $C_{30}H_{38}O_4$, the latter into sugar and *helleboretin*, $C_{14}H_{20}O_3$.

Glycyrrhizin, exists in the liquorice-root. It is a white powder, which is decomposed by acids into dextrose and *glycyrrhetin*, a resinous body.

Digatalin, is the active principle of *Digitalis purpurea*. It forms small colorless crystals very slightly soluble in water, easily in hot alcohol and chloroform. Dilute acids decompose it into sugar and *digitalretin*, an amorphous substance. On warming with concentrated chlorhydric or phosphoric acid, it assumes a beautiful green color.

Coloring Matters.

Some of the more important coloring matters occurring in nature, the constitution of which is accurately known, as well as some of those which have been produced synthetically, have already been mentioned, *e.g.*, indigo-blue and alizarine. Coloring matters are of both vegetable and animal origin. In the former case, they do not usually exist already formed, but united with sugar as ethers, and are set free by fermentation,

and by the action of dilute acids and alkalis. The substances occurring in plants are, hence, glucosides, and are called, when the substance united with the sugar is a coloring matter, *chromogenes*.

The coloring matters all belong to the aromatic series. They possess in general weak acid properties, are soluble in alkalis with a peculiar color which is not usually that of the free coloring matter, and form insoluble compounds with metallic oxides, particularly with the oxides of lead, tin, iron, and alumina, as well as with animal, and occasionally vegetable fibres.

Dyeing depends on the animal or vegetable fabric, either by itself or impregnated with a solution of aluminum acetate, lead oxide, etc., attracting the dissolved coloring matter and forming with it an insoluble compound.

When the dye deposited on the fibres is insoluble in acids and alkalis it is called "fast," but when acted on, it is designated "not fast," or "fugitive." Owing to the different degrees of solubility of the coloring matters, this classification is naturally very imperfect.

Coloring matters are decomposed by oxidizing agents. The ozone and hydrogen peroxide of the air, or, better still, chlorine, decompose almost all coloring matters, or as it is expressed, "bleach" them (chlorine-bleach, grass-bleach).

Sulphurous acid bleaches many coloring matters, particularly those of animal origin, forming with them colorless compounds, which, however, are decomposed by strong acids (sulphuric acid) with regeneration of the color.

A great number of coloring matters which occur in nature have been produced by artificial means, *e.g.*, the aniline colors, eosine, naphthalene-yellow, etc.

A series of homologous compounds, which are anhydride compounds of acids, occur in the lichens. Most of them yield on decomposition orcinol, $C_7H_8O_2$ (see p. 249), which with ammonia, forms *lichen-red*, or *orcein*. The *Rocella tinctoria* contains *orsellic acid*, $C_{16}H_{14}O_7$, the salts

of which when boiled with water yield *orsellinic acid*, $C_8H_8O_4$. Orsellinic acid decomposes into orcinol $C_7H_8O_2$, and carbonic acid.

As the constitution of orcinol is $C_6H_3\begin{cases}(OH)_2,\\CH_3\end{cases}$ orsellinic acid is :

$$C_6H_2\begin{cases}(OH)_2\\CH_3\\COOH\end{cases},$$

and orsellic acid is the anhydride of orsellinic acid :

$$O\begin{cases}C_6H_2(CO_2H)(CH_3)OH\\C_6H_2(CO_2H)(CH_3)OH\end{cases}.$$

Evernic acid, $C_{17}H_{16}O_7$, occurs in the *Evernia prunastri*. On boiling with alkalis, it breaks into *everninic acid*, $C_9H_{10}O_4$, and orsellinic acid, $C_8H_8O_4$:

$$C_{17}H_{16}O_7 + H_2O = C_9H_{10}O_4 + C_8H_8O_4.$$

Everninic acid has the constitution, $C_6H_2\begin{cases}OH\\OCH_3\\CH_3\\COOH\end{cases}$. Evernic acid is hence :

$$O\begin{cases}C_6H_2(COOH)(CH_3)(OCH_3)\\C_6H_2(COOH)(CH_3)(OH)\end{cases}.$$

Usnic acid, $H_{19}C_{18}O_7$, exists in numerous lichens (*cladonia*, *evernia*, *parmelia* and *usnea*). Its last decomposition-product is *betaorcinol*, $C_8H_{10}O_2$.

Betaorcinol is probably, $C_7H_5\begin{cases}(OH)_2\\CH_3\end{cases}$. Usinic acid is hence :

$$O\begin{cases}C_7H_4(CO_2H)(CH_3)(OH)\\C_7H_4(CO_2H)(CH_3)(OH)\end{cases}.$$

The *Rocella fuciformis* contains *erythric acid*, $C_{20}H_{22}O_{10}$, which, on boiling with alkalis, splits into orsellinic acid, $C_8H_8O_4$, and *picroerythrin*, $C_{12}H_{16}O_7$. The latter on continued boiling with alkalis, is decomposed into carbonic acid, orcinol, $C_6H_3\begin{cases}(OH)_2\\CH_3\end{cases}$, and erythrol, (p. 138), $C_4H_{10}O_4$.

Picroerythric acid is hence the erythrol compound of orsellinic acid : $C_6H_2\begin{cases}CO_2H\\CH_3\\OH\\O\text{-}C_4H_9O_3\end{cases}$, and erythric acid is therefore :

$$O\begin{cases} C_6H_2(CO_2H)(CH_3)(O^-C_4H_9O_3) \\ C_6H_2(CO_2H)(CH_3)(OH) \end{cases}.$$

All of the lichen-acids (orsellic, evernic, usnic, and erythric), except evernic acid, are crystalline compounds. They are colored red by calcium hypochlorite, or on exposure to the air in presence of ammonia. Orcinol is the final product of the action of alkalis on all of them.

Vulpinic acid, $C_{19}H_{14}O_5$, exists in *Cetraria vulpina*. On boiling with barium hydroxide, it is resolved into alphatoluic acid, $C_6H_5{}^-CH_2{}^-CO_2H$ (p. 262), methyl alcohol and oxalic acid :

$$C_{19}H_{14}O_5 + 4\ H_2O = \underset{\text{Alphatoluic acid}}{2\ C_8H_8O_2} + \underset{\text{Oxalic acid}}{C_2H_2O_4} + CH_4O.$$

It forms with alkalis and alkaline earths, yellow or orange-colored salts which are soluble in water.

Log-wood (*Hæmatoxylon campechianum*) contains *hæmatoxylin :*

$$C_{16}H_{14}O_6 + 3\ H_2O,$$

which can be extracted with water. It forms yellow, transparent prisms with a sweet taste, and soluble in alkalis with a purplish-red color. Its solution in ammonia oxidizes rapidly in the air, being converted into the ammonium salt of a red coloring matter, *hæmateïn*, $C_{16}H_{10}O_5$.

The solution becomes continually darker red. The hæmateïn can be precipitated by acetic acid.

Santalin, $C_{15}H_{14}O_5$, exists in sandal-wood. It forms microscopic red crystals, which dissolve in alkalis with a violet color.

Brasilin, $C_{16}H_{14}O_5$, exists in Brazil-wood. When pure it forms almost colorless prisms, which become first yellow and finally carmine-red when exposed to the air. It dissolves in dilute sodium hydroxide lye with a beautiful carmine-red color. The alkaline solution is bleached by acids. It is oxidized by nitric acid to trinitroresorcinol, and on dry distillation it yields resorcinol abundantly. In alkaline solution, it is oxidized when exposed to the air into *brasileïn*, $C_{16}H_{12}O_5$, which forms silvery, glittering leaflets dissolving in alkalis with a purplish-red color.

Safflor (flowers of the *Carthamus tinctorius*) contains both a yellow and a red coloring matter. The latter, *carthamin*, $C_{14}H_{16}O_7$, is a dark-red powder with a green reflex, soluble in alkalis with a yellowish-red color, and in this solution not stable. When fused with potassium hydroxide, it yields protocatechuic acid, $C_6H_3(CO_2H)(OH)_2$.

Polychroït, $C_{15}H_{60}O_{15}$, exists in saffron (*Crocus sativus*). It is an

orange-red substance which is resolved by acids into sugar, an oxygenated oil, $C_{10}H_{14}O$, and a red body, *crocin*, $C_{16}H_{18}O_8$:

$$C_{48}H_{60}O_{18} + H_2O = 2\,C_{16}H_{18}O_8 + C_{10}H_{14}O + C_6H_{12}O_6.$$

In tumeric, a yellow coloring matter called *curcumin*, $C_{14}H_{14}O_4$, occurs. On oxidation with potassium dichromate and sulphuric acid, it yields acetic and carbonic acids, while by incomplete oxidation with potassium permanganate, vanillin (methyl ester of protocatechuic aldehyde) is produced. Di-ethylcurcumin affords ethylvanillin. Curcumin is hence :

$$C_6H_3\begin{cases}1\ CH(C_6H_5)COOH\\3\ OCH_3\\4\ OH\end{cases}$$

It forms stout needles fusing at 178°, and soluble in alkalis and alkaline carbonates with a brownish-red color. Paper colored yellow with curcumin is turned brownish-red by alkaline liquids, and on drying becomes violet. Acids turn it yellow again. When tumeric paper is moistened with a solution of boracic acid and dried, it turns orange-red. This color is not affected by acids, but is turned blue by alkalis.

In the cochineal, the female of an insect (*Coccus cacti*) and in the flowers of the *Monarda didyma*, a red coloring matter, *carminic acid*, $C_{17}H_{18}O_{10}$, occurs. On boiling with dilute acids, it breaks into *carmine-red*, $C_{11}H_{12}O_7$, and a species of sugar, $C_6H_{10}O_5$. On heating with concentrated sulphuric acid at 150°, it evolves carbonic acid, and is oxidized into *ruficoccin*, $C_{16}H_{12}O_6$:

$$C_{17}H_{18}O_{10} + O = C_{16}H_{12}O_6 + CO_2 + 3\,H_2O.$$

Boiled with nitric acid, it is converted into *nitrococcussic acid :*

$$C_8H_5(NO_2)_3O_3.$$

Nitrococcussic acid is a tri-nitro-cresotic acid, $C_8H_8O_3$, and its constitution is hence :

$$C_6(NO_2)_3(CH_3)(OH)(CO_2H).$$

The constitution of ruficoccin is probably :

$$C_{14}H_{12}\begin{cases}(CH_3)_2\\(OH)_4\\O_2\end{cases},$$

i.e., the tetra-hydroxylated quinone of dimethylanthracene.

The most widely distributed coloring matter is the green matter of leaves, and is called *chlorophyll*. But little is as yet known about it. It appears to be a mixture of a yellow and a blue coloring matter. In autumn, the blue substance disappears, and, as the leaves contain then only the yellow coloring matter, they appear yellow.

Bitter Principles.

The so-called bitter principles are closely related to the coloring matters and lichen-substances. They have an intensely bitter taste. A number of glucosides are sometimes placed in this class. The bitter substances are the active principles of many important medicinal plants.

Aloïn, $C_{15}H_{16}O_7$, is the active constituent of aloes. It forms small colorless crystals with a sweetish, bitter taste, and varying percentage of water. It easily becomes amorphous. On warming with nitric acid, it yields *chrysammic acid* (tetranitro-chrysazin, p. 304), $C_{14}H_2(NO_2)_4O_2(OH)_2$, which crystallizes in golden-yellow, difficultly soluble leaflets, decomposing by fusion with potassium hydroxide into oxalic acid, orcinol, paroxybenzoic acid, and *aloretic acid*, $C_9H_{10}O_3 + H_2O$ (fine needles fusing at 115°).

Santonin, $C_{15}H_{18}O_3$, exists in worm-seed, and forms colorless, pearly, glittering leaflets very difficultly soluble in water, quite easily soluble in alcohol, and fusing at 170°. It is the anhydride of *santonic acid*, $C_{15}H_{20}O_4$, into which it is very easily converted by bases. *Sodium santonate*,

$$C_{15}H_{19}NaO_4 + 3\,H_2O,$$

forms colorless rhombic crystals. Acids decompose it, setting free santonic acid. The acid passes very easily into santonin. Both santonin and sodium santonate, turn yellow on standing exposed to the light.

Picrotoxin, $C_{21}H_{14}O_5$, is contained in the seed of the

Menispermus cocculus. It crystallizes in glittering needles, somewhat soluble in water. It reduces alkaline cupric solutions and is poisonous.

Cetrarin, $C_{18}H_{16}O_8$, which occurs in Iceland moss, crystallizes in needles insoluble in water, easily soluble in alcohol. It dissolves in alkalis and alkaline carbonates with a yellow color.

Quassiin, $C_{10}H_{12}O_3$, is the bitter principle of quassia-wood. It forms colorless leaflets with an extremely bitter taste. It is but little soluble in water, easily soluble in alcohol.

Absynthin ($C_{20}H_{28}O_4$?), is produced from worm-wood, *Artemisia absynthium.* It is a very bitter substance with the odor of worm-wood.

A large number of the substances of this class have been already mentioned under glucosides.

The following acrid principles are intimately related to the bitter principles.

Cantharidin, $C_{10}H_{12}O_4$, is the active principle of the Spanish-fly. It crystallizes in colorless columns, and when pure is insoluble in water. It produces blisters on the skin.

Cossin, $C_{26}H_{22}O_5$, is the active principle of the cosso. It is yellow powder with a peculiar odor and a bitter, harsh taste. It is difficultly soluble in water, easily in alcohol, ether, and alkalis.

Betulin, $C_{36}H_{60}O_3$, exists in the bark of the birch. It crystallizes in large, thin prisms fusing at 251°, insoluble in water and difficultly in alcohol and ether.

Carotin, $C_{18}H_{24}O$, is found in minute crystals in the cells of the yellow carrot. The carrot owes its color to the presence of this substance. It crystallizes in reddish-brown cubes, fusing at 168°, is insoluble in water, difficultly in alcohol, and possesses a fragrant odor.

Chrysin, $C_{15}H_{10}O_4$, is contained in the buds of the poplar.

It forms bright-yellow tablets fusing at 275°, insoluble in water, difficultly soluble in alcohol and ether, and more easily in alkalis, forming with the latter an intense yellow solution.

Ostruthin, $C_{28}H_{34}O_4$, is found in the roots of the *Imperatoria ostruthium*. It crystallizes in colorless needles fusing at 115°. Its alcoholic solution exhibits a blue fluorescence. Alkalis dissolve it with a yellow color.

Peucedanin, $C_{10}H_{16}O_4$, occurs in the roots of the *Peucedanum officinale*, and forms colorless prisms fusing at 76°. Alcoholic potassa, or concentrated chlorhydric acid, decomposes it into *oreoselon*, $C_{14}H_{12}O_4$, which crystallizes in needles fusing at 177°.

Cascarillin, $C_{12}H_{18}O_4$, is found in cascarilla-bark. It crystallizes in colorless, bitter prisms fusing at 205°, difficultly soluble in water and easily in hot alcohol.

Columbin, $C_{21}H_{22}O_7$, occurs in the columbo-root, and forms colorless, bitter prisms.

Smilacin, $C_{18}H_{30}O_6$, exists in sarsaparilla. It crystallizes in colorless prisms, which are slightly soluble in hot water, forming a strongly foaming solution with an offensive taste.

Biliary Substances.

Before passing to the description of the more important parts of the animal organism, we shall take up the properties and metamorphoses of several compounds which occur in them.

The chief constituents of the bile are the potassium and sodium salts of two acids, viz., *glycocholic* and *taurocholic acids*.

Glycocholic acid, $C_{26}H_{43}NO_6$, forms fine needles, almost insoluble in water, easily soluble in alcohol, and possessing a sweet taste and an acid reaction. It is a monobasic acid. When mixed with a solution of sugar, and then treated with concen-

trated sulphuric acid, it yields a deep purplish-red solution. On boiling with dilute acids, it is resolved into glycocoll, $C_2H_5NO_2$ (p. 98), and *dyslysin*, $C_{24}H_{36}O_3$:

$$C_{26}H_{43}NO_6 = C_2H_5NO_2 + C_{24}H_{36}O_3 + H_2O.$$

Dyslysin is an amorphous body, insoluble in water. When glycocholic acid is boiled with alkalis, it splits into glycocoll and *cholic acid*, $C_{24}H_{40}O_5$:

$$C_{26}H_{43}NO_6 + H_2O = C_2H_5NO_2 + C_{24}H_{40}O_5.$$

Cholic acid crystallizes with $2\frac{1}{2}H_2O$, in colorless, glassy octahedrons which are insoluble in water.

Taurocholic acid, $C_{26}H_{45}NSO_7$, forms colorless needles easily soluble in water and alcohol. Its solution turns the plane of polarized light to the right. On boiling with water, or more quickly with dilute acids or alkalis, it is decomposed into cholic acid, $C_{24}H_{40}O_5$, and *taurin*, $C_2H_7NSO_3$ (p. 82):

$$C_{26}H_{45}NSO_7 + H_2O = C_{24}H_{40}O_5 + C_2H_7NO_3S.$$

Both glycocholic and taurocholic acids exist in varying proportions in the bile of almost all animals. To this the bile of the pig is an exception, as it contains two other acids, the *hyoglycocholic* and *hyotaurocholic* acids.

Hyoglycocholic Acid, $C_{27}H_{43}NO_5$, is a colorless amorphous mass, which is insoluble in water and easily soluble in alcohol. Its salts taste bitter. Its alkali salts are soluble in water, its others insoluble. It is resolved by boiling with dilute acids or alkalis, into glycocoll, $C_2H_5NO_2$, and *hyocholic acid*, $C_{25}H_{40}O_4$:

$$C_{27}H_{43}NO_5 + H_2O = C_2H_5NO_2 + C_{25}H_{40}O_4.$$

Hyocholic acid forms warty crystals insoluble in water.

Hyotaurocholic Acid, $C_{27}H_{45}NO_6$, exists in only very small amounts in the bile of the pig. It breaks on treatment with alkalis, into taurin, $C_2H_7NSO_3$, and hyocholic acid, $C_{25}H_{40}O_4$.

The bile contains, besides the two acids mentioned, another constituent, viz., *cholesterin*. Cholesterin, $C_{26}H_{44}O$, exists also in the blood, brain, and yolks of eggs. It occasionally occurs in such amounts in the bile that it separates, forming what are known as "gall-stones." It is the chief constituent of the fat of wool. It has been proved to exist also in plants. It crystallizes in colorless, glittering leaflets or silky needles, with one molecule H_2O, fusing at 145°, boiling at 360°. Insoluble in water, and soluble in alcohol. It is an alcohol, and forms a chloride, $C_{26}H_{43}Cl$, ether, etc.

The bile contains certain coloring matters to which it owes its peculiar color, golden-yellow in man and grass-green in herbivora. *Bilirubin*, $C_{16}H_{18}N_2O_3$, is a bright-red powder which changes to brown on exposure to the air. It is insoluble in water and alcohol, but in alkalis it is very easily soluble, with an orange-red color, which on very great dilution is yellow. In the disease known as icterus, it causes the yellow color of the skin. It absorbs oxygen and becomes green, which accounts for the golden-yellow color of bile turning to green when exposed to the air. The bilirubin is hereby changed into *biliverdin*, $C_{16}H_{18}N_2O_4$, a blackish-green powder, insoluble in water and soluble in alcohol. It is colored yellow by sulphurous acid. Both bilirubin and biliverdin, when treated in alkaline solution with ordinary nitric acid, which always contains nitrous acid, give characteristic color-reactions. The solution becomes green, and passes through blue, violet, ruby-red into a dirty-yellow.

Gall-stones, contain a small amount of *bilifuscin*, $C_{16}H_{20}N_2O_4$, a brittle, glittering almost black mass. The following coloring matters are also found in bile, but in small amounts. *Biliprasin*, $C_{16}H_{22}N_2O_6$, a glittering, almost black mass. *Bilihumin*, a blackish-brown powder which is formed from the other biliary coloring matters on exposure of their alkaline solutions to the air.

Proteïn Substances.

A number of very highly constituted substances, some solid and some in solution, occur in animal and vegetable organisms. They are very intimately related to each other, and

are called *proteïn, proteïds, albuminous substances,* and *albuminoids.* They all contain carbon, hydrogen, oxygen, nitrogen, and sulphur. The various kinds show small differences in composition from each other, but our methods of analysis are not delicate enough to enable us to assign them even an empirical formula.

In plants, the proteïn bodies are contained in far less amounts than the carbhydrates, but in the animal kingdom they form the chief part of the organic constituents. They are formed, however, only in the plant, and are introduced into the animal organism through plant-food, being only assimilated and further changed by the animal.

They exist either in solution (vegetable and animal liquids) or undissolved, in a soft, moist state, as organized structures, or amorphous, as the coagulum in liquids. Their being in solution in plants and animal structures is owing to the presence of small amounts of bases, acids, or salts. They can be precipitated from these solutions by boiling, or by alkalis, acids, and various salts. Precipitated in this manner, they form usually an amorphous, flocculent, soft, odorless and tasteless mass, which when dried is transparent and brittle. It is insoluble in pure water, but soluble in dilute alkalis. They are very unstable, being slightly decomposed even by precipitating from a solution and redissolving. When kept in a moist state, they decompose quickly, becoming putrid, and yielding a great number of less highly constituted bodies (carbonic acid, volatile fatty acids, fats, lactic acid, ammonia, amine bases, ammonium sulphide, leucine, tyrosine, etc.). Putrefying albuminous substances impart their chemical activity to many other substances, thus acting as ferments, or starting fermentation. They are resolved by reduction with stannous chloride and chlorhydric acid into leucine, $C_6H_{13}NO_2$, tyrosine, $C_9H_{11}NO_3$, asparaginic acid, $C_4H_7NO_4$, and an acid homologous with asparaginic acid, *glutamic acid*, $C_5H_9NO_4$.

Tyrosine, *Hydroxyphenylamidopropionic Acid:*

$$C_9H_{11}NO_3 = C_6H_4(OH)^-C_2H_3(NH_2)COOH,$$

is a decomposition-product of albuminous substances, and is hence found in putrefying animal liquids, rotten cheese, etc. It is a white, crystalline powder, very difficultly soluble in cold water, but more easily in hot. It is an amic acid, and unites with both acids and bases. It is hence easily soluble in alkalis and dilute acids. It yields a nitro-product with nitric acid, and with sulphuric acid, a sulphonic acid.

Albumin is recognized by the following reactions :

On warming with concentrated nitric acid, it becomes yellow (xanthoproteïn reaction).

On boiling with a solution of mercuric nitrate and then adding a trace of nitrous acid, it becomes red (Millon's reaction).

Treated with concentrated sulphuric acid and then with a solution of sugar, it becomes red and then violet-red.

On boiling for some time with concentrated chlorhydric acid, in which it dissolves on heating, it affords an intense violet-red solution.

All of the albumins go into solution when digested with the acid juice of the stomach at 30–40°, producing the so-called *peptones*, which are really a mixture of leucine, tyrosine, etc., and no longer albuminous substances.

There are four classes of albuminous bodies, the differences between which, however, are very slight.

1) **Albumin,** *Egg-albumin*, *Serum-albumin*, *Vegetable-albumin*, and *Globulin*. They are precipitated (coagulated) by warming their solutions to 60–70°.

2) **Caseïn,** *Animal-caseïn*, and *Plant-caseïn* (*Legumin*). They are coagulated by the mucous membrane of the stomach of the calf (rennet).

3) **Fibrin,** *Blood-fibrin*, *Muscle-fibrin* (*Myosin*), and *Gluten*. They become insoluble as soon as they have left the organism.

4) **Proteïds,** *Hæmoglobin*, and *Vitellin*. They are resolved by various agents into albumin and other substances.

Albumins. The albumins occur in the juices of plants, and can be extracted from the dried plants with cold water. They also occur in the whites of birds' eggs, in the milk of animals, in the plasma of the blood, chyle, lymph, in the serous liquids, juices of the muscles, animal semen, and in the nutritive liquids. In all cases, it is held in solution by the salts

contained in the liquids, and can always be precipitated by dilution with a large amount of water.

Solutions of albumin become turbid at 60°, and at 75° the whole of the albumin separates in white flocks (coagulation).

If only a small amount of salts or acids is present, a lower temperature is sufficient to precipitate the albumin. But if small amount of alkalis is present, a higher temperature is required for coagulation. Strongly alkaline or acid solutions of albumin are not precipitated by heating.

Hydrogen sulphide is set free during the coagulation of albumin. Coalgulated albumin is insoluble in water.

A solution of albumin which has been strongly acidified (*e.g.* with chlorhydric acid of 0.2%), loses its property of coagulating, but coagulates on neutralization with a base. The solution contains the so-called *acid-albumin.*

When coagulated albumin is treated with concentrated potassa, a solid elastic jelly is obtained, which on washing loses alkali until a constant composition has been attained. This albumin is called *alkali-albumin,* and is insoluble in cold water, soluble in hot, its solution remaining clear after cooling. The animal and plant organisms contain many albumins in the form of alkali-albumins.

A peculiar modification of albumin exists in the crystalline lens of the eye, and is called *Crystallin.* It also occurs in small amounts in the white of egg, chyle, etc., and is termed *Globulin.* It is precipitated from its solution by carbonic acid as a white powder.

Among the substances resembling albumin, are *Paralbumin,* which exists in dropsical ovaries, is only partly precipitated by boiling, and is soluble in water ;

Pancreatin, which is contained in the juice of the pancreas ;

Ptyalin, which exists in the saliva ;

Diastase, which is found in germinating barley.

The last three convert starch into sugar.

Caseïn. The caseïns are alkali-albumins which are precipitated by alcohol, metallic salts, and acids. The pure solutions do not coagulate on boiling, except after addition of calcium chloride, calcium sulphate, magnesium sulphate, etc. The natural solutions (milk) coagulate (curdle) slowly on exposure to the air, because lactic acid is formed from the milk-sugar. They are also coagulated by calf-rennet, probably owing to the presence of a ferment in it.

The animal caseïn exists chiefly in milk. The vegetable caseïn (legumin) occurs principally in the almonds and leguminosæ.

Fibrin is found in the blood, chyle, lymph, and in many serous exudations. The blood coagulates (clots) after removal from the animal organism, the coagulum, or clot, being the fibrin. By beating the blood with a glass rod, it can be obtained in a fibrous state. It forms a white, tough, amorphous mass.

Fibrin does not exist as such in blood, but is formed by the union of paraglobulin and fibrinogen. The paraglobulin is contained in the red-blood corpuscles and diffuses out of them into the liquid of the blood (plasma), being found, after the coagulation of the blood, in the remaining serum, as it is present in large amounts. It is precipitated from its solutions by carbonic acid, and resembles globulin very much.

The muscles contain a liquid (muscle-protoplasm) which after death coagulates and becomes solid (*rigor mortis*). The insoluble body thus separated, is called *myosin*, or *flesh-fibrin*.

The vegetable substance analogous to fibrin is known as *gluten*. It can be obtained by kneading wheat-flour on a sieve with water. The starch is washed through, and the gluten remains. It is a mixture of various substances, gluten-fibrin, gluten-caseïn, mucedin, and gliadin.

Proteïds. The red color of the blood is due to the presence of a red coloring-matter. This substance can be obtained in

microscopic, but beautifully formed crystals, and is called *Hæmoglobin.* It crystallizes with hydrate-water, which it gradually loses on exposure to the air, and dissolves in water to a red liquid. On boiling this solution with alcohol, a rusty colored precipitate separates, which, after washing out with acidified alcohol, becomes colorless, and is albumin. The coloring matter, which is soluble in acidified alcohol, is called hæmatin.

Hæmatin contains iron. On heating it is decomposed, and on igniting in the air it leaves a residue of pure ferric oxide. Its composition is $C_{34}H_{34}N_4O_5Fe$.

The hæmoglobin effects the absorption of gases by the blood. It absorbs oxygen with avidity, and gives it up again as soon as another gas (*e.g.* carbonic acid) is passed through it to saturation. It takes up ozone from substances containing it, and gives it up again as oxygen. On taking up oxygen, its color becomes brighter red, while with carbonic acid it becomes dark red. Hence blood containing oxygen (arterial blood) is bright-red, while blood containing carbonic acid (venous blood), is dark.

It unites with carbonous oxide, forming a crystalline bluish-red compound, which is more stable than oxygenated hæmoglobin. With nitrogen di-oxide and cyanhydric acid it forms compounds which are more stable than with carbonous oxide.

The three compounds just mentioned, CO, NO, and HCN, are hence powerful poisons, and produce death because they render the hæmoglobin incapable of taking up oxygen.

Hæmatin, which is the decomposition-product of hæmoglobin, is a bluish-black powder, insoluble in water, alcohol, and ether, and soluble in alkalis, ammonia, and dilute acids. It forms with chlorhydric acid, a crystalline compound, which is used as a characteristic test for the presence of blood.

If a fragment of dried blood is placed on the object-glass of a microscope, a grain of salt added, then covered with a glass plate, the powder

moistened with a drop of glacial acetic acid and warmed till the acetic acid begins to evolve bubbles, and then allowed to cool, the field will be found to be filled with minute black crystals of hæmatin.

The spectrum of a hæmoglobin solution shows two absorption-bands, which have, however, different positions, depending on whether the hæmoglobin is saturated with oxygen, nitric oxide, or carbonous oxide.

In the yolks of eggs, there is a substance which, besides the elements common to albumins (C, H, N, O, and S), contains phosphorus, viz., *Vitellin*. It is decomposed by warm alcohol with the separation of albumin, while another substance, *Lecithin*, which contains all the phosphorus of the vitellin remains in solution.

Lecithin, $C_{42}H_{84}NPO_9$, is a peculiar glyceride. It forms a crystalline mass easily soluble in alcohol, which, on boiling with dilute acids, or alkalis, is resolved into oleïc acid, $C_{18}H_{34}O_2$, palmitic acid, $C_{16}H_{32}O_2$, neurin, $C_5H_{15}NO_2$, and glycerylphosphoric acid, $C_3H_7O_2 . H_2PO_4$ (see p. 119).

Neurin, which can be produced artificially by heating trimethylamine, $(CH_3)_3N$, with glycolchlorhydrin,

$$CH_2(OH)^-CH_2Cl,$$

has the constitution :

$$CH_2(OH)^-CH_2N(CH_3)_3OH.$$

It is an ammonium base, the nitrogen of which is united with three methyl-groups, one hydroxyl-group and the di-valent rest of glycol (glycol minus OH). It crystallizes in deliquescent needles which possess strong basic properties, attract carbonic acid from the air, and on boiling, break into tri-methylamine and glycol. It forms finely crystallizable salts with acids. On oxidation, it is converted into *oxyneurin*, $C_5H_{13}NO_3$, which occurs in the red-beet (*Beta vulgaris*). It is made

artificially by the action of trimethylamine on monochloracetic acid, $CH_2Cl^-CO_2H$. Its constitution is hence,

$$COOH^-CH_2^-N(CH_3)_3OH.$$

It forms large deliquescent crystals with basic properties.

From the above-mentioned facts, it is possible to derive the constitution of lecithin. It is glycerol in which 2 H's are replaced by the rest of oleïc and palmitic acids, and a third H by the rest of phosphoric acid, while an H of the phosphoric acid rest is replaced by the rest of neurin :

$$\begin{array}{l} CH_2^-O^-C_{18}H_{33}O \\ | \\ CH^-O^-C_{16}H_{31}O \\ | \\ CH_2^-O^-PO\begin{array}{l}OH \\ O^-CH_2^-CH_2^-N(CH_3)_3OH.\end{array} \end{array}$$

As has already been stated, the composition of the various proteïds can only be expressed in percentages, and not by chemical formulas. The following will serve as examples :

Egg-albumin	Blood-albumin	Vegetable-albumin	Blood-fibrin	Vegetable-fibrin
C = 53.4 %	53.0 %	53.4 %	52.6 %	53.4 %
H = 7.0 %	7.1 %	7.1 %	7.0 %	7.1 %
N = 15.6 %	15.6 %	15.6 %	17.4 %	15.6 %
O = 22.4 %	23.1 %	23.0 %	21.8 %	22.8 %
S = 1.6 %	1.2 %	0.9 %	1.2 %	1.1 %

Milk-caseïn	Legumin-caseïn	Almond-caseïn	Hæmoglobin
C = 53.6 %	51.5 %	50.8 %	53.8 %
H = 7.1 %	7.0 %	6.7 %	7.3 %
N = 15.7 %	16.8 %	18.4 %	16.1 %
O = 22.6 %	24.3 %	23.7 %	21.9 %
S = 1.0 %	0.4 %	0.4 %	0.5 %
			Fe = 0.4 %.

We come now to a series of nitrogenous bodies which are intimately related to the proteïn substances proper, and which are derived from them, but which differ from them in containing much less carbon. They possess the general name of **Albuminoids.**

In many pathological conditions, the cells and tissues suffer a peculiar change and assume a waxy consistency. A sub-

stance is hereby formed which is colored reddish-brown by iodine, and green or blue when first moistened with concentrated sulphuric acid. As these reactions resemble those of starch (amylum), this substance is called *amyloid*. It is a colorless, crumbly mass, insoluble in water, alcohol, and ether. It passes with difficulty into putrefaction.

Animal connective tissues, on continued boiling with water, form a clear solution, which, when cool, solidifies to a soft elastic mass. This gelatinizing substance is called *glue*. There are two species of glue, viz.: glutin and chondrin.

Glutin is obtained by boiling bones, tendons, skins, etc., with water. It forms, when dry, a colorless, transparent, brittle mass, which swells up in water, and at 40° absorbs water without dissolving. It forms a thin solution when boiled with water, which gelatinizes on cooling. It loses the property of gelatinizing, if boiled repeatedly with water, more quickly when boiled with dilute acids, or by heating to 140° with water in closed vessels.

It is precipitated from its solution by alcohol and tannic acid. Concentrated sulphuric acid decomposes it, forming, besides other products of decomposition, chiefly glycocoll and leucine. In the moist state, it passes easily into putrefaction.

Chondrin is prepared by boiling young bones, which are still soft, and cartilage with water. It resembles glutin very much, and is only distinguishable by its being precipitated from its aqueous solution by dilute acids and the salts of iron, copper, lead, and silver. It is not precipitated by mercuric chloride. By the action of sulphuric acid, leucine only and no glycocoll is produced. It is also decomposed by concentrated chlorhydric acid, a fermentable sugar, *chondroglucose*, being produced among other substances.

The horny tissues, *e.g.*, hair, wool, feathers, nails, claws, talons, hoofs, horns, epidermis, epithelium, etc., contain as a chief constituent, *keratrin*. Keratrin does not form a glue

with water, but dissolves when digested with it at 150°, yielding a clear solution which does not gelatinize on cooling.

Hair and wool contain considerable sulphur (about 5%), a part of which is so loosely combined, that it will unite with lead or silver. This explains the blackening of the hair when combed with a lead or silver comb.

Mucin exists in the saliva, mucus, bile, synovia, urine, semen, excrement, and glands. It is a colorless, opaque, flocculent mass, which, on drying, becomes brittle and horny. It is insoluble in water, but swells up in it. It is soluble in a dilute salt solution. Its solution is glairy and ropy, and foams on shaking. It does not contain sulphur.

Elastin is the basis of the elastic tissues. In a moist state, it is very elastic, insoluble in water, dilute acids and alkalis. When dry, it is hard and brittle, but swells up when placed in water. On boiling with sulphuric acid, it yields leucine, but no tyrosine.

Silk-fibrin is an albuminoid, and the chief constituent of silk. It is a white, glittering mass, insoluble in water, and soluble in alkalis and concentrated acids. On boiling with dilute sulphuric acid, it yields leucine, tyrosine, glycocoll, and sugar.

The important difference between vegetable and animal life consists in the former producing highly constituted compounds from simpler substances; as carbonic acid, ammonia, water, etc., which are taken up from the earth and atmosphere. Animals, on the other hand, consume the compounds built up by plants, and decompose them into the original simple compounds. Plant life is a synthetic and reduction process (plants principally inhale carbonic acid and exhale oxygen), while animal life is an analytical and oxidation process (animals inhale oxygen and exhale carbonic acid).

Appendix.

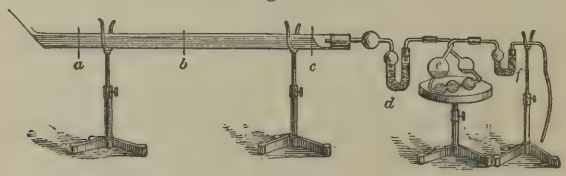
There are two methods by which the constitution of a compound can be determined. Both of them are usually employed. Complicated substances are decomposed by simple reactions into simpler bodies, the constitution of which is known, or more complicated compounds are produced from simple substances of known structure. The former method is the analytic, the latter the synthetic. Both of the methods will be described, but it is first necessary to explain the methods for the determination of the percentage composition and molecular weight of compounds.

Determination of the Composition of Organic Substances.

Estimation of Carbon and Hydrogen.—Carbon and hydrogen are always estimated in a single operation. As it has already been stated in the introduction, the carbon is oxidized to carbonic acid and the hydrogen to water. Two substances rich in oxygen are used as oxidizing agents, viz., cupric oxide, CuO, and plumbic chromate, $PbCrO_4$, or a mixture of both. The combustion is effected in a tube of difficultly fusible glass 60–70 cm. long (Fig. 1). The glass tube is drawn out at one end into a narrow tube turned up at an obtuse angle and the end closed by fusing. The tube is half filled with freshly ignited, perfectly dry cupric oxide, or plumbic chromate (to *b*), and a weighed amount of the substance mixed in by means of a brass rod which is bent at the end in the form of a corkscrew. The remainder of the tube is then filled with cupric

oxide and closed with a tightly fitting cork through which passes a U-tube filled with calcium chloride (*d*); the calcium chloride absorbs the water formed by the combustion. Connected with this tube, is a peculiar bulb-apparatus (*e*) (Liebig-bulb), which serves to absorb the carbonic acid. It is filled with a concentrated solution of potassium hydroxide, and connected with a small U-tube (*f*) which is filled with small pieces of potassium hydroxide, which absorb the last traces of carbonic acid, and also take up any moisture which may be carried from the potassa solution by the stream of gas.

Fig. 1.



By gently tapping the tube, a canal is formed for the evolution of the gaseous products of combustion. The tube is then placed in the combustion furnace and heated.

Figure 1 represents the combustion tube filled and ready for analysis. Fig. 2 shows the whole apparatus.

Up to *a* is pure cupric oxide;
a–b is the mixture of the substance and cupric oxide;
b–c is again pure cupric oxide;
d is the calcium chloride tube;
e is the bulb-apparatus filled with potassium hydroxide solution;
f is the tube filled with solid potassium hydroxide.

Both the calcium chloride tube and the potash-bulbs are weighed before the combustion. The tube is gradually heated to a red heat, beginning at *c* and advancing slowly, till the whole tube is heated. The operation is observed by the passage of the bubbles through *e*. When the combustion is ended, the potassa solution rises in the bulb nearest the calcium chloride

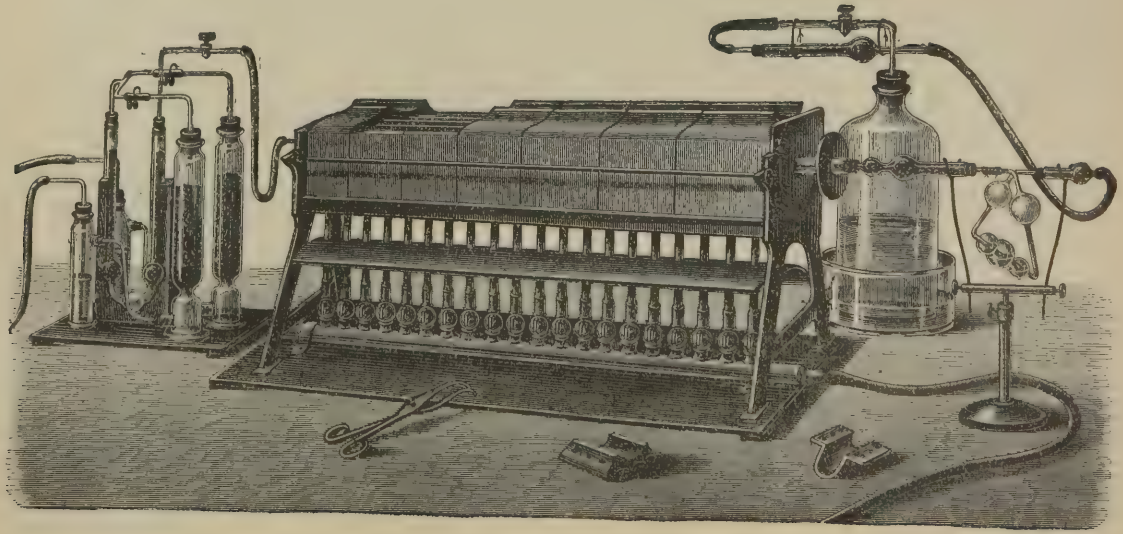


Fig. 2.

tube. The flames are then extinguished, the point of the tube broken, and air, which has been freed from carbonic acid and moisture by passing through a solution of potassium hydroxide and over calcium chloride, is drawn through the tube in order to remove the last traces of moisture and carbonic acid remaining in it. The calcium chloride tube and the potash-bulbs are then again weighed, and the differences between the first and last weights give the amounts of moisture and carbonic acid which have been formed by the combustion of the hydrogen and carbon in the substance.

The weight of water obtained is to the weight of hydrogen in the substance as $H_2O : H_2$, or as 18 : 2, or as 9 : 1, *i.e.*, the weight of the hydrogen is $\frac{1}{9}$ of the weight of water found. The relation between the carbonic acid and the carbon is as $CO_2 : C$, or as 44 : 12, or as 11 : 3. The weight of the carbon is hence $\frac{3}{11}$ of the weight of the carbonic acid found.

If the substance to be analyzed is a liquid, it is introduced into a small glass bulb, Fig. 3, by placing the point under the surface of the liquid and warming the bulb. On cooling, the liquid rises and fills the bulb. The point is then fused. The combustion tube is filled to *a* with cupric oxide, the bulb thrown in with such force that it is broken, the remainder of the tube then filled with cupric oxide, and the operation carried out as in the preceding case.

Fig. 3.



If the substance contains, besides carbon and hydrogen, nitrogen, a part of the oxygen of the cupric oxide unites with the nitrogen, forming NO, which is absorbed with the carbonic acid, by the potassa, thus rendering the determination of the carbonic acid valueless. In this case, a layer of metallic copper is placed in the front part of the tube. Copper possesses the property of decomposing NO at a red heat, setting free the nitrogen and uniting with the oxygen.

The layer of metal should fill about 10 cm., and should,

previously to its use, be ignited and cooled in a stream of dry hydrogen.

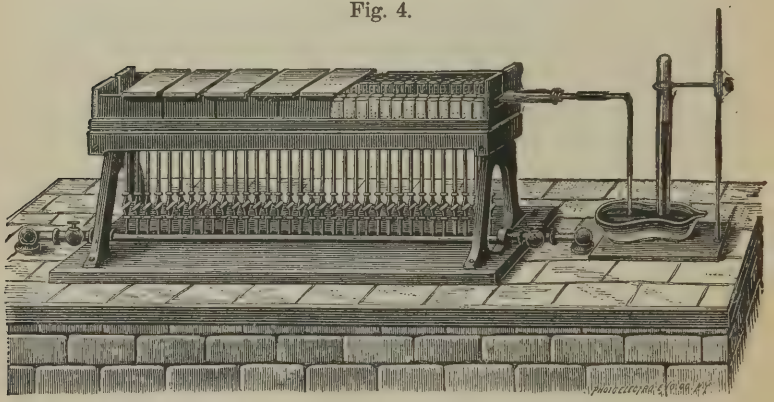
When the substance contains chlorine, bromine, iodine, sulphur, or phosphorus, it cannot be burnt with cupric oxide. In this case, plumbic chromate must be used, and the first three or four flames must be kept low, so that the end of the tube next to the calcium chloride tube does not become heated to a full red.

Estimation of Nitrogen.—In most cases the nitrogen in organic substances can be converted into ammonia (the exceptions are nitro-compounds and certain organic amides). The substance is heated with soda-lime (a mixture of equal parts of caustic soda and lime), in a tube of difficultly fusible glass, the operation being carried out as in the ordinary combustion. Ammonia is evolved and absorbed by leading into dilute chlorhydric acid, and determining the ammonium chloride formed by conversion into platinic ammonium chloride, $(NH_4Cl)_2PtCl_4$. The ammonia can also be absorbed by a measured amount of a standard acid, and the amount neutralized determined by titration with a standard alkali. If the nitrogen is in the form of a nitro-group, it is estimated in the following manner : The substance is burnt, as just described, with cupric oxide and metallic copper, but in the end of the tube, a layer of about 5 cm. of magnesium carbonate is placed. After this follow the layer of cupric oxide, the mixture of the substance with cupric oxide, another layer of cupric oxide, and finally the spirals of metallic copper. The open end of the tube is then closed with a cork through which passes a tube bent as shown in Fig. 4, which passes under the surface of the mercury contained in the bath, and under the end of the eudiometer, or graduated glass tube. On top of the column of mercury in the eudiometer, a layer of a solution of potassium hydroxide is placed. The magnesium carbonate is first heated carefully, till carbonic acid is freely evolved and all the air is expelled from the tube. This is shown by the complete absorption of the bub-

bles by a solution of potassium hydroxide, which is conveniently contained in a test-tube inverted over the delivery tube.

When the bubbles are completely absorbed, the tube is heated, beginning at the delivery-end and proceeding carefully toward the closed end. The gas evolved is received in the eudiometer. When no more gas is given off, the layer of

Fig. 4.



magnesium carbonate is again heated till the bubbles are completely absorbed by the potassium hydroxide solution. The gas contained in the eudiometer is pure nitrogen. The eudiometer is then placed in a tall vessel filled with water, and after standing some time, the volume of the gas is noted. From the volume of gas thus obtained, its weight is calculated, due observance being made for the temperature, content of moisture, and the pressure of the atmosphere.

The formula for calculating the weight of a given volume of nitrogen is

$$P = \frac{0.001256 \times V \times (B-f)}{760 \times (1 + 0.00367t)}.$$

P denotes the weight of nitrogen sought ;

V denotes the observed volume of the gas in cubic centimeters ;

B denotes the barometric pressure ;

f denotes the tension of the vapor of water at the temperature t ;

t denotes the temperature at the time of the observation ;

0.001256 is the weight of 1 c.c. of nitrogen at 0° C. and 760 mm. barometric pressure ;

760 is the normal barometric pressure ;

0.00367 is the coefficient of expansion for a gas for one degree Centigrade.

Chlorine, Bromine, and Iodine are estimated by two methods.

1) The substance is mixed with pure caustic lime and ignited in a short combustion tube. The mass, after cooling, is diffused in water and dissolved in nitric acid, the solution filtered, and the halogen precipitated and weighed in the form of its corresponding silver salt.

2) The substance is heated with twenty to thirty times its volume of concentrated nitric acid and some solid silver nitrate, in a closed tube at 100°–300° for several hours. The hydrogen and oxygen of the substance are completely oxidized into carbonic acid and water, while the halogen unites with the silver. After cooling, the tube is opened carefully, the contents washed out with water, filtered, and the insoluble silver chloride, etc., weighed as usual.

Sulphur and Phosphorus are also estimated in two ways.

1) The substance is ignited with a mixture of four parts of sodium carbonate, and one part of potassium nitrate. The sulphur and phosphorus are oxidized, forming sodium sulphate and phosphate. The sulphuric acid of the sulphate is precipitated as barium sulphate with barium chloride, and the phosphoric acid as ammonium magnesium phosphate with magnesium chloride and ammonia.

2) The substance is heated in a closed tube at 100° to 300° with 20–30 times its volume of concentrated nitric acid. The sulphur and phosphorus are oxidized into sulphuric and phosphoric acids, and are estimated by the usual methods.

The other constituents of organic compounds are estimated, after the destruction of the organic substance, by the usual methods of analytical chemistry.

It has been stated in the introduction that the simplest way to determine the molecular weight of a substance, is to compare the weight of a certain volume of its gas with the same volume of air or hydrogen. As the atomic weight of hydrogen is taken as unity, it is more advisable to compare the volume-weights of all substances with it, for the molecular weight is then obtained by simply doubling the number found. As pressure and temperature, however, exercise an important influence on the expansion of gases, it is necessary to reduce the volume found to 0° and the normal atmospheric pressure (760 mm.), and to compare it with hydrogen measured under the same conditions. One c.c. of hydrogen at 0° and under 760 mm. pressure weighs 0.0000896 gm.

Fig. 5.

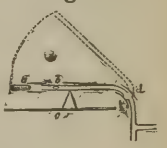


Fig. 6.



The specific weight of a body is estimated by two methods, viz.: either by determining the volume of a known weight of a substance, or by determining the weight of a known volume of the substance.

Fig. 7.



The first method is carried out in two ways. (1) The apparatus consists of a flask *c* (Fig. 5), in which is placed the tube *b* of a capacity of about 100 c.c. and about 200 mm. high, which terminates in a glass tube 600 mm.

long and about 6 mm. in diameter, ending in a stopper-neck. About 100 mm. from the end, a tube, *a*, is fused on.

A weighed amount of the substance, sufficient to give not more than 50 c.c. of vapor, is placed in the small tube *b*, and dropped into the main tube by means of the device shown in Fig. 6. On pressing the wire *f* of the support, *d* is removed, and the tube *e* falls. In Fig. 7 the object is accomplished by having the end of the main tube movable by means of the rubber connection *d*. On elevating the movable arm *a*, the small tube *b* falls into the heating tube. A piece of cardboard, *c*, is affixed to the under side of the movable arm, to prevent the heating of the substance. Depending on the temperature necessary, the flask *c* is filled with water, xylene, aniline, ethyl benzoate, amyl benzoate, diphenylamine, etc. For heating above 310° a bath of melted lead is used. When very high temperatures (1,500–1,600°) are required, the apparatus is made of porcelain.

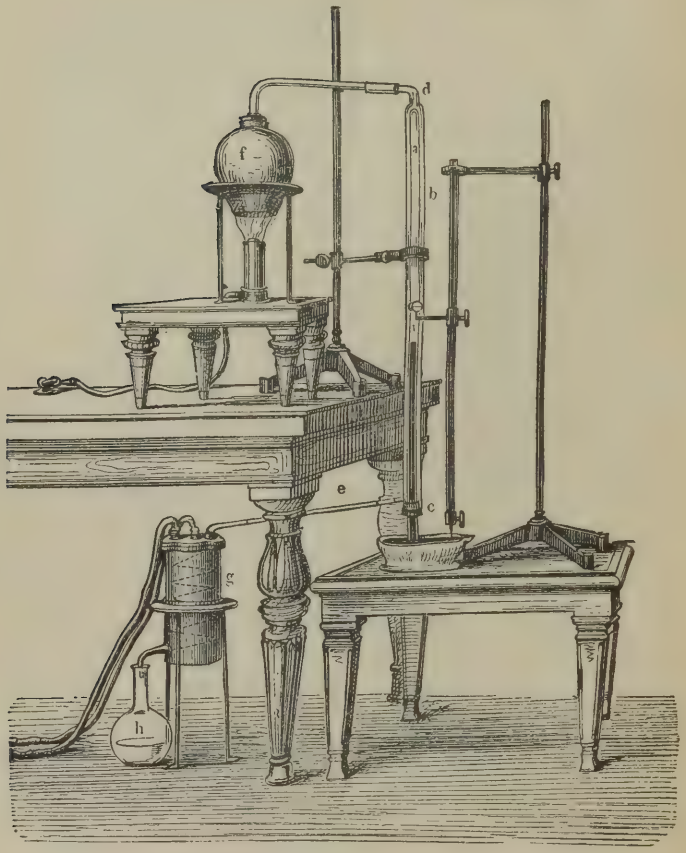
The operation is conducted as follows: The tube *b* is heated till no more bubbles of air issue at *f*, and the temperature remains constant. The substance is then allowed to fall into the tube, and the air which is displaced by the vaporization of the substance is collected in a graduated tube. When no more bubbles appear, the graduated tube is placed in a tall vessel of water, and after the temperature of the air and the water have become the same, the levels of the water within and without the tube are brought to the same point, and the volume of gas read off.

The weight of the gas is calculated by the following formula:

$$D = S \cdot \frac{(1 + 0.003665 \cdot t) \cdot 587780}{(B - w) \cdot V} .$$

S is the weight of the substance;
B is the barometric pressure reduced to 0°;
w is the tension of the vapor of water at $t°$;
V is the volume of air.

Fig. 8.



(2) A graduated tube *a*, one meter long (Fig. 8), is filled with mercury and inverted over mercury, so that a barometric vacuum of about 25 cm. exists in it, and the height of the column of mercury standing over the surface of the mercury in the bath estimated.

A weighed amount of the substance, contained in a small flask (Fig. 9), is then placed in the tube. The tube is next covered with the large tube *b*, which is contracted above into a small tube, bent at a right angle and connected with a flask, *f*, filled with water, turpentine (boiling at 160°), or aniline (boiling at 185°). The whole apparatus is steadied by a stand. The liquid in the flask is now heated. The vapor fills the outside tube, bringing it to its own temperature. The substance in the inner tube is vaporized, pressing the mercury down. As soon as the level of the mercury remains constant, the operation is finished.

Fig. 9.



The volume of gas is read off, the height of the column of mercury again measured, its volume found at the temperature of the vapor (100°, 160°, or 185°), and the observed barometric pressure reduced to the temperature of 0° and 760 mm. pressure. The height of the mercury above the surface of the mercury in the bath is ascertained by means of a measuring apparatus, which consists of a brass rod containing an iron pendant divided into millimeters, moved by a screw, and terminating in a steel point. The brass rod is suspended from the stand by means of a universal joint.

The vapor density of a gas compared with hydrogen is calculated by the following formula :

$$D = \frac{760 \times (273 + t') \times p}{V \times 273 \times 0.0000896 \times B} .$$

$$B = \frac{b}{1 + 0.00018t} - \left(\frac{b'}{1 + 0.00018t} + \frac{b''}{1 + 0.00018t'} + s \right) .$$

D is the vapor density sought (100,° 160,° 185,° etc) ;
t' is the temperature of the vapor ;
t is the temperature of the room ;
p is the weight of the substance taken ;
V is the observed volume in c.c. ;
B is the height of the barometer ;
b' the height of the column of mercury not heated by the vapor ;
b'' the height of the column of mercury heated by the vapor ;

$b' + b''$ is the height of the column of mercury above the level of the surface of the mercury in the bath, after attaining a constant point (a''), at the temperature t';

760 is the normal height of the barometer;

$273 + t'$ is the expansion of the gas by the rising temperature;

0.0000896 is the weight of one cubic centimeter of hydrogen;

$1 + 0.00018t$ is the expansion of liquid mercury from the temperature t. It expands 0.00018 of its volume for every degree C.

The gas-volume weight of all bodies which boil under 250° can be estimated by this method. For substances boiling at

Fig. 10.

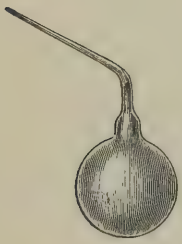


Fig. 11.

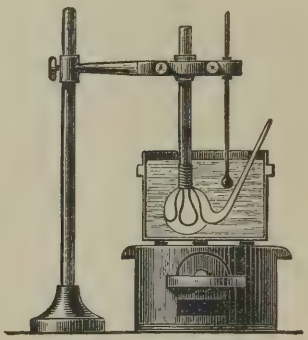


Fig. 12.



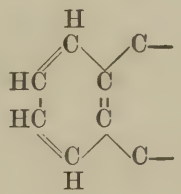
higher temperatures, the second method can be used where the first modification of the first method is not desirable.

A small glass balloon, holding about 200–300 c.c. (Fig. 10), is drawn out to a fine point and bent upwards. About five grams of the substance are placed in the balloon, which is then heated in a bath of easily fusible alloy to a temperature about 20–30° above the boiling point of the substance. The temperature must be kept constant for some time, so that the vapors of the substance may drive all the air out of the balloon and fill it *completely*. The end of the fine tube of the balloon, which projects from the bath, is then fused, and the balloon removed from the bath, cooled, and weighed.

The point is then broken under mercury, which at once fills the vacuum. The amount of mercury required to fill the balloon is determined. To obtain the weight of the glass, the weight of the air is subtracted from the weight of the balloon filled with air. The weight of the volume of the gas at a known temperature is obtained by subtracting the weight of the glass from the weight of the balloon filled with the gas. The volume of gas is then reduced to 0° and 760 mm. pressure.

Analytical method for the determination of the constitution of compounds.—This method consists in decomposing a compound into simpler substances of known constitution, or into substances of the same carbon content of known constitution.

When we find that naphthalene, for instance, yields phthalic acid on oxidation, it is proved that naphthalene contains a benzene nucleus ; and, further, that two carbon atoms of the benzene chain are united with hydrocarbon rests instead of with hydrogen. A portion of the structure of naphthalene is thus shown to be



The elimination of carbonic acid from organic acids by heating with lime, or sodium hydroxide, is an analytical method. Acetic acid yields methane when distilled with lime, while benzoic acid affords benzene by the same treatment :

$$\underset{\text{Acetic acid}}{C_2H_4O_2} = \underset{\text{Methane}}{CH_4} + CO_2$$

$$\underset{\text{Benzoic acid}}{C_7H_6O_2} = \underset{\text{Benzene}}{C_6H_6} + CO_2.$$

It follows, therefore, that benzoic acid has the same relation to benzene, as acetic acid to methane. Since acetic acid may be supposed to be derived from methane by the replacement of an atom of hydrogen by a carboxyl-group, benzoic acid can be derived from benzene by the replacement of an H by COOH.

CH_4, Methane, $CH_3{}^-COOH$, Acetic acid.
C_6H_6, Benzene, $C_6H_5{}^-COOH$, Benzoic acid.

In this manner the constitution of many aromatic acids has been determined. Catechuic acid, $C_7H_6O_4$, for instance, yields on distillation by itself, or better, with lime, pyrocatechol. Pyrocatechol has the constitution, $C_6H_4(OH)_2$. Hence catechuic acid must have the constitution, $C_6H_3\left\{\begin{matrix}(OH)_2\\CO_2H\end{matrix}\right.$. Gallic acid has the composition, $C_7H_6O_5$. By elimination of carbonic acid, pyrogallic acid, $C_6H_6O_3$, or $C_6H_3(OH)_3$, is obtained. Hence gallic acid has the constitution:

$$C_6H_2\left\{\begin{matrix}(OH)_3\\CO_2H\end{matrix}\right.$$

This method for the elimination of carbonic acid affords also a method of producing new compounds. All the compounds which bear the name of "pyro" have been formed from other substances by elimination of carbonic acid, viz.: pyromucic acid, pyromellitic acid, pyroracemic acid, pyrocatechol, etc.

Oxidation frequently affords an insight into the constitution of a substance, and constitutes a second analytical method. The oxidation of an alcohol shows whether it is primary, secondary, or tertiary; for the primary alcohols yield on oxidation, aldehydes; the secondary, ketones; and the tertiary are decomposed into acids of lower carbon content.

In the same way, the constitution of the ketones can often be ascertained. Ketones are decomposed by oxidation into

acids of lower orders (p. 113), the CO-group remaining with the lesser hydrocarbon rest.

Methyl-butylketone, $CH_3{-}CO{-}C_4H_9$, yields acetic and butyric acids on oxidation:

$$\underset{\text{Methylbutylketone}}{CH_3{-}CO{-}C_4H_9} + 3\,O = \underset{\text{Acetic acid}}{CH_3{-}COOH} + \underset{\text{Butyric acid}}{C_4H_8O_2}.$$

While the isomeric ketone, ethyl-propylketone, yields only propionic acid:

$$\underset{\text{Ethylpropylketone}}{C_2H_5{-}CO{-}C_3H_7} + 3\,O = \underset{\text{Propionic acid.}}{C_2H_5{-}COOH} + C_3H_6O_2.$$

The aromatic hydrocarbons homologous with benzene, *i.e.*, containing side-chains, are, as a rule, easily oxidized. The whole side-chain breaks off, leaving one carboxyl united with the benzene nucleus. The atom of carbon of the side-chain, which is united to the benzene nucleus, is oxidized to carboxyl, while the other atoms of the side-chain are oxidized to acids of the fatty series (see p. 231).

$$\underset{\text{Toluene}}{C_6H_5{-}CH_3} + 3\,O = \underset{\text{Benzoic acid}}{C_6H_5{-}CO_2H} + H_2O$$

$$\underset{\text{Ethylbenzene}}{C_6H_5{-}CH_2{-}CH_3} + 6\,O = \underset{\text{Benzoic acid}}{C_6H_5{-}CO_2H} + CO_2 + 2\,H_2O$$

$$\underset{\text{Propylbenzene}}{C_6H_5{-}CH_2{-}CH_2{-}CH_3} + 5\,O = \underset{\text{Benzoic acid}}{C_6H_5{-}CO_2H} + \underset{\text{Acetic acid}}{CH_3{-}CO_2H} + H_2O.$$

All homologues of benzene having only one side-chain yield benzoic acid on oxidation. In the same way, all homologues of benzene having two side-chains give dicarboxylic acids (one of the three phthalic acids) on oxidation.

$$\underset{\text{Dimethylbenzene}}{C_6H_4\begin{cases}CH_3\\CH_3\end{cases}} + 6\,O = \underset{\text{Phthalic acid}}{C_6H_4\begin{cases}CO_2H\\CO_2H\end{cases}} + 2\,H_2O$$

$$\underset{\text{Methylethylbenzene}}{C_6H_4\begin{cases}CH_3\\CH_2CH_3\end{cases}} + 9\,O = \underset{\text{Phthalic acid}}{C_6H_4\begin{cases}CO_2H\\CO_2H\end{cases}} + CO_2 + 3\,H_2O$$

$$\underset{\text{Diethylbenzene}}{C_6H_4\begin{cases}C_2H_5\\C_2H_5\end{cases}} + 12\,O = \underset{\text{Phthalic acid}}{C_6H_4\begin{cases}CO_2H\\CO_2H\end{cases}} + 2\,CO_2 + 4\,H_2O.$$

The products obtained by the oxidation show clearly, therefore, the number and nature of the side-chains.

The constitution of a substance can often be determined in exactly the opposite way, viz.: by reduction. In this way the sulphonic acids are distinguished from the isomeric alkylsulphurous acids. The former yield with nascent hydrogen, mercaptan; the latter, alcohols and hydrogen sulphide:

$$\underset{\text{Methylsulphonic acid}}{CH_3{}^-SO_2OH} + 6\,H = \underset{\text{Methylmercaptan}}{CH_3SH} + 3\,H_2O$$

$$\underset{\text{Methyl sulphurous acid}}{CH_3{}^-O^-SO_2H} + 6\,H = \underset{\text{Methyl alcohol}}{CH_3OH} + 2\,H_2O + H_2S.$$

In a similar manner, the nitro-compounds are easily distinguished by reduction, from the isomeric nitrous esters. The former give amido-compounds, the latter, alcohols:

$$\underset{\text{Nitromethane}}{CH_3NO_2} + 6\,H = \underset{\text{Methylamine}}{CH_3NH_2} + 2\,H_2O$$

$$\underset{\text{Methyl nitrous ester}}{CH_3{}^-O^-NO} + 6\,H = \underset{\text{Methyl alcohol}}{CH_3OH} + NH_3 + H_2O.$$

There are no other general methods for the determination of the constitution of substances analytically. The constitution of many compounds can, however, be ascertained by conversion into simpler compounds of known constitution. As examples, we may recall uric acid (p. 167), creatine (p. 171), the glucosides (p. 329), the lichen principles (p. 333), etc.

The synthetic method for the examination of the molecular structure of compounds consists in starting out from simple compounds of known constitution, and building up from them more complicated substances in such a manner that the reactions can be accurately followed, and the constitution of the bodies formed determined.

The synthesis of organic compounds, from their elements, constitutes here a particular class. By passing the vapor of ammonium carbonate, which is easily sublimable, over fused potassium, potassium cyanide is formed. Potassium cyanide is converted by oxidizing agents (minium), into potassium cyanate. Potassium cyanate, on boiling with a solution of ammonium sulphate, is transposed into urea. Ammonium cyanate is first formed and then converted into urea by atomic migration.

$$2\,KCNO + (NH_4)_2SO_4 = K_2SO_4 + 2\,NH_4{}^-CNO.$$

$$NH_4{}^-CNO = CO\begin{cases} NH_2 \\ NH_2 \end{cases} \text{ Urea.}$$

Hydrogen sulphide and carbon disulphide, when passed over heated copper form methane :

$$2\,H_2S + CS_2 + 4\,Cu_2 = 4\,Cu_2S + CH_4.$$

By the action of chlorine on methane, methyl-chloride, CH_3Cl, is formed, from which all the derivatives of methane can be obtained ; from it, also, compounds of higher carbon content can be built up.

When electric sparks are passed between poles of carbon in an atmosphere of hydrogen, acetylene is formed. Acetylene, C_2H_2, treated with nascent hydrogen yields ethylene, C_2H_4, and ethane, C_2H_6, from which all the derivatives of ethane can be obtained. By leading acetylene through a red-hot tube, benzene is formed :

$$3\,C_2H_2 = C_6H_6,$$

from which an infinity of aromatic compounds can be produced.

Synthesis, in its broadest sense, means the artificial production of an organic compound from another. We shall have occasion later on, under the action of reagents on organic substances, to mention the methods by which it can be effected.

In a stricter sense, we understand by synthesis, the joining together of hydrocarbon rests by means of their carbon atoms. Strictly speaking, the production of ether is not a synthetic process, because the binding of the two rests is effected by oxygen :

$$CH_3OH + CH_3OH = CH_3{}^-O{}^-CH_3 + H_2O.$$

The formation of methyl cyanide from methyl iodide, is, on the other hand, a true synthesis :

$$CH_3I + CNK = CH_3{}^-CN + KI.$$

The principal methods for the production of compounds rich in carbon from those poor in carbon are the following :

1. The sodium compound of an organic substance is treated with the halogen compound (alkylogen, *i.e.* chloride, bromide, or iodide), sodium chloride, etc., being formed, and the two rests uniting :

$$CH_3Na + CH_3Br = \underset{\text{Ethane}}{CH_3{}^-CH_3} + NaBr$$

$$C_2H_5Na + CH_3Br = \underset{\text{Propane}}{C_2H_5{}^-CH_3} + NaBr.$$

A very large number of organic compounds have been produced by this method.

By acting with sodium on an ester (compound ether), hydrogen is set free, and a sodium compound is formed, in which the sodium is united to the carbon atom. The compound thus obtained, when treated with an alkylogen, yields the ester of an acid richer in carbon :

$$2\,CH_3{}^-COOC_2H_5 + 2\,Na$$
$$= \underset{\text{Ethyl sodiumaceto-acetic ester}}{CH_3{}^-CO{}^-CHNa{}^-COOC_2H_5} + C_2H_5ONa + H_2.$$

$$CH_3{}^-CO{}^-CHNa{}^-COOC_2H_5 + C_2H_5Br$$
$$= NaBr + \underset{\text{Aceto-ethylacetic ethylester}}{CH_3{}^-CO{}^-\overset{\overset{C_2H_5}{|}}{C}H{}^-COOC_2H_5}.$$

Potassium hydroxide not only saponifies the acetoacetic ethylester, but decomposes it according to another reaction. In one reaction, acetic acid and a second acid are formed, while in the other, carbonic acid and a ketone are formed :

a) $CH_3\text{-}CO\text{-}CH(C_2H_5)\text{-}COOC_2H_5 + 2\,KOH = CH_3\text{-}COOK + \underset{\text{Potassium butyrate}}{C_2H_5\text{-}CH_2\text{-}COOK} + C_2H_5OH.$

b) $CH_3\text{-}CO\text{-}CH(C_2H_5)\text{-}COOC_2H_5 + KOH = \underset{\text{Methyl-propyl-ketone}}{CH_3\text{-}CO\text{-}CH_2\text{-}C_2H_5} + CO_2 + C_2H_5OH.$

Instead of ethyl bromide, the chloride or iodide of any hydrocarbon, aci-chlorides, bromides, etc., and chlorinated, brominated, etc., esters can be used, so that an almost unlimited series of acids and ketones can be produced.

In many cases it is not necessary to make the sodium compound, in order to eliminate the halogen and join the rests together, it being sufficient to treat two chlorides, bromides, or iodides with sodium :

$$CH_3I + CH_3I + Na_2 = \underset{\text{Ethane}}{CH_3\text{-}CH_3} + 2\,NaI$$

$$CH_3I + C_2H_5Br + Na_2 = \underset{\text{Propane}}{CH_3\text{-}C_2H_5} + NaBr + NaI$$

$$C_6H_5Br + CH_3I + Na_2 = \underset{\text{Methylbenzene}}{C_6H_5\text{-}CH_3} + NaBr + NaI$$

$$C_6H_5Br + C_2H_6Br + Na_2 = \underset{\text{Ethylbenzene}}{C_6H_5\text{-}C_2H_5} + 2\,NaBr$$

$$C_6H_5Br + C_6H_5Br + Na_2 = \underset{\text{Diphenyl}}{C_6H_5\text{-}C_6H_5} + 2\,NaBr.$$

Many hydrocarbons, particularly of the aromatic series, have been obtained in this way.

2. By leading carbonic acid through the sodium compound of a hydrocarbon, the carboxylic acid of the next higher series is formed :

$$CH_3Na + CO_2 = \underset{\text{Sodium acetate}}{C_2H_3NaO_2} = CH_3{}^{-}CO_2Na.$$

By leading carbonic acid over the sodium salt of a phenol, the corresponding acid of the next higher carbon series is obtained :

$$\underset{\text{Sodium phenoxide}}{2\,C_6H_5ONa} + CO_2 = \underset{\text{Sodium salicylate}}{C_6H_4\begin{cases}ONa\\COONa\end{cases}} + C_6H_5OH.$$

Analogous to this reaction, is the formation of the corresponding aldehyde of a higher carbon series by digesting the alkaline solution of a phenol with chloroform, the chloroform acting as formic acid in *statu nascendi :*

$$C_6H_5OH + CHCl_3 + 3\,NaOH$$
$$= \underset{\text{Sodium salicylaldehyde}}{C_6H_4(ONa)^{-}CHO} + 3\,NaCl + 2\,H_2O.$$

In this case, also, it is frequently only necessary to pass the carbonic acid through the bromide or iodide of the hydrocarbon in presence of sodium :

$$C_6H_5Br + Na_2 + CO_2 = \underset{\text{Sodium benzoate}}{C_6H_5{}^{-}COONa} + NaBr.$$

3. The halogen derivatives of the hydrocarbons of the fatty series, or the sulphonic acids of the aromatic series, when distilled with potassium cyanide, yield the cyanide of the hydrocarbon. In this case also, the union is through carbon. These cyanides, on boiling with potassium hydroxide, are converted into the acids, the CN-group passing into the COOH-group :

$$CH_3I + KCN = CH_3{}^{-}CN + KI.$$
$$CH_3{}^{-}CN + 2\,H_2O = \underset{\text{Acetic acid}}{CH_3{}^{-}CO_2H} + NH_3.$$

$$\begin{matrix}CH_2Br\\ |\\ CH_2Br\end{matrix} + 2\,KCN = \begin{matrix}CH_2{}^{-}CN\\ |\\ CH_2{}^{-}CN\end{matrix} + 2\,KBr.$$

Ethylene bromide — Ethylene cyanide

$$\begin{matrix}CH_2{}^{-}CN\\ |\\ CH_2{}^{-}CN\end{matrix} + 4\,H_2O = \begin{matrix}CH_2{}^{-}CO_2H\\ |\\ CH_2{}^{-}CO_2H\end{matrix} + 2\,NH_3.$$

Ethylene cyanide — Succinic acid

4. The action of the zinc compounds of the hydrocarbons on the alkylogens is analogous to that of the sodium compounds:

$$COCl_2 + Zn\langle{}^{CH_3}_{CH_3} = ZnCl_2 + CO\langle{}^{CH_3}_{CH_3}$$

Phosgen — Zinc methyl — Acetone

or

$$2\,COCl_2 + Zn\langle{}^{CH_3}_{CH_3} = ZnCl_2 + 2\,COCl{}^{-}CH_3$$

Phosgen — Zinc methyl — Acetyl chloride

also a) $$CH_3{}^{-}COCl + Zn(CH_3)_2 = CH_3{}^{-}C\langle{}^{OZnCH_3}_{CH_3}{}_{Cl}$$

b) $$CH_3{}^{-}C\langle{}^{OZnCH_3}_{CH_3}{}_{Cl} + Zn(CH_3)_2$$

$$= CH_3{}^{-}C\langle{}^{OZnCH_3}_{CH_3}{}_{CH_3} + ZnCH_3Cl$$

c) $$CH_3{}^{-}C\langle{}^{OZnCH_3}_{CH_3}{}_{CH_3} + 2\,H_2O$$

$$= CH_3{}^{-}C(OH)\langle{}^{CH_3}_{CH_3} + Zn(OH)_2 + CH_4$$

Trimethylcarbinol

5. In the presence of aluminic chloride, the aromatic hydrocarbons unite with the chlorides derived from the alcohols with evolution of chlorhydric acid, forming new hydrocarbons:

$$C_6H_6 + CH_3Cl = HCl + C_6H_5CH_3$$
$$C_6H_6 + 2\,CH_3Cl = 2\,HCl + C_6H_4(CH_3)_2$$
$$C_6H_6 + 3\,CH_3Cl = 3\,HCl + C_6H_3(CH_3)_3 \text{ etc.}$$

6. Aromatic compounds unite with aldehydes in the presence of concentrated sulphuric acid, forming substances richer in carbon :

$$2\,C_6H_6 + CH_3{}^-CHO = H_2O + \underset{\text{Diphenylethane}}{CH_3{}^-CH(C_6H_5)_2}, \text{ etc.}$$

7. Salts of organic acids (the lime salts are best) when submitted to dry distillation, either alone or with the salts of other organic acids, afford ketones richer in carbon :

$$2\,CH_3CO_2Na = \underset{\text{Acetone}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CO} + Na_2CO_3.$$
Sodium acetate

$$CH_3{}^-CO_2Na + C_2H_5{}^-CO_2Na = \underset{\text{Methyl-ethyl ketone}}{\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>\!CO} + Na_2CO_3.$$
Sodium acetate Sodium propionate

As a peculiar kind of synthesis, *condensation* may be mentioned. Condensation is the union of two or more molecules of one or more substances by means of their carbon atoms, accompanied by the elimination of water. Aldehydes and ketones, in particular, exhibit this reaction.

Aldehyde, C_2H_4O, when treated with weak dehydrating agents (*e.g.*, chlorhydric acid), is converted into

Crotonic aldehyde, C_4H_6O :

$$2\,C_2H_4O = C_4H_6O = CH_3{}^-CH{=}CH{}^-CHO + H_2O.$$

Benzaldehyde, $C_6H_5{}^-CHO$, and aldehyde, in a similar manner pass into cinnamic aldehyde, C_9H_8O :

$$C_7H_6O + C_2H_4O = C_9H_8O = C_6H_5{}^-CH{=}CH{}^-CHO + H_2O.$$

The formation of collidine, $C_8H_{11}N$, from ethylidene

chloride and ammonia, also belongs here, although the nascent chlorhydric acid eliminates ammonia:

$$4\,CH_3{-}CHCl_2 + 4\,NH_3 = \underset{\text{Hypothetical body}}{4\,CH_3{-}CH{=}NH} + 8\,HCl.$$

$$4\,CH_3{-}CH{=}NH = \underset{\text{Collidine}}{C_8H_{11}N} + 3\,NH_3.$$

Acetone yields with chlorhydric acid the condensation-products, mesityl oxide, $C_6H_{10}O$, and phorone, $C_9H_{14}O$:

$$2\,\underset{\text{Acetone}}{C_3H_6O} = \underset{\text{Mesityl oxide}}{C_6H_{10}O} + H_2O.$$

$$\underset{\text{Acetone}}{C_3H_6O} + \underset{\text{Mesityl oxide}}{C_6H_{10}O} = \underset{\text{Phorone}}{C_9H_{14}O} + H_2O.$$

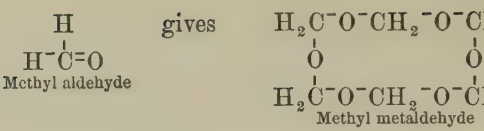
Phorone does not yield further condensation products by an elimination of water; the hydrocarbon, mesitylene, C_9H_{12}, is formed (p. 266).

The formation of rosolic acid by the oxidation of a mixture of phenol and salicyl aldehyde, rosanilines by the oxidation of a mixture of aniline and toluidine, and the phthaleïnes (p. 264) by the action of phthalic anhydride on phenols at an elevated temperature, or in presence of sulphuric acid, belong to this class.

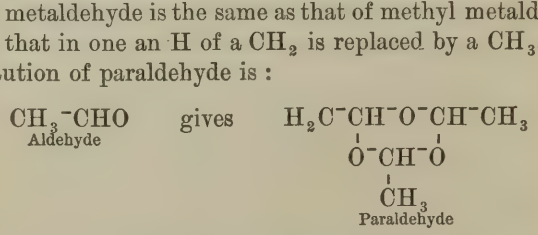
Polymerization, although not properly a form of synthesis, should be mentioned under the head of condensation. It consists usually in three molecules of a simply constituted body uniting to one molecule. When the carbon atom of a compound is united by more than one bond to a polyvalent atom, this binding can be dissolved to a simple one, and the molecules thus having free attractive energies, unite among themselves to one molecule.

Aldehydes, cyanic acid, CONH, and its derivatives, and cyan chloride yield, in particular, polymerization-products.

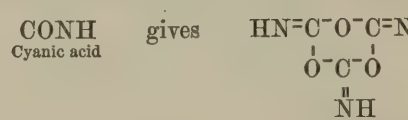
Methaldehyde, CH_2O, (p. 29) passes into methyl metaldehyde ($C_6H_{12}O_6$?), the constitution of which is probably:



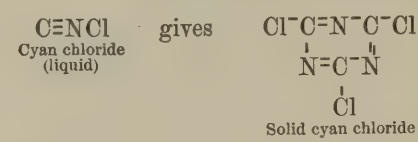
Ethyl aldehyde yields the trimolecular paraldehyde, and probably also the hexamolecular metaldehyde. The constitution of metaldehyde is the same as that of methyl metaldehyde, except that in one an H of a CH_2 is replaced by a CH_3. The constitution of paraldehyde is :



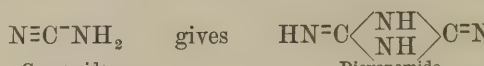
Cyanic acid passes into the trimolecular cyanuric acid :



Liquid cyan chloride yields solid cyan chloride :

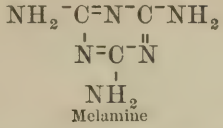


Two molecules, probably, of cyanamide polymerize to dicyanamide :

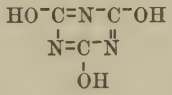


The polymerization of three molecules, forms melamine, $C_3H_6N_6$:

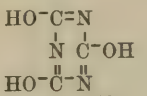

Cyanamide

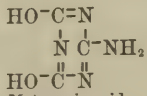

Melamine

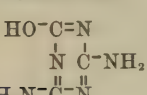
The constitution of the isomeric cyanuric acid may be analogous to that of melamine:

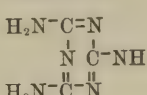


It has not been ascertained whether the cyanuric acid known has this formula, or whether its nitrogen binds single molecules together. If we accept this formula, we can deduce a number of compounds which stand between cyanuric acid and melamine, and which can be supposed to be derived from each other by substitutions of the OH by NH_2, viz., cyanuric acid, $C_3H_3N_3O_3$, melanuric acid, $C_3H_4N_4O_2$, ammeline, $C_3H_5N_5O$, and melamine, $C_3H_6N_6$.


Cyanuric acid


Melanuric acid


Ammeline


Melamine

Action of Reagents on Organic Compounds.

As the ordinary reagents usually act on organic compounds in a characteristic manner, it is possible to establish certain rules for their action.

1) *Chlorine, Bromine* and *Iodine,* act substitutingly:

$$CH_4 + Cl_2 = CH_3Cl + HCl$$
$$C_6H_6 + Br_2 = C_6H_5Br + HBr.$$

It is necessary, however, in the case of iodine, to destroy at once the iodohydric acid which is formed, else it will cause an inverse substitution, and thus prevent the substitution by the iodine. It is therefore necessary in cases where iodine is to be introduced directly, to add nitric acid, or iodic acid, if the former disturbs the reaction, in order to at once decompose the iodohydric acid, which is formed, into iodine:

$$HIO_3 + 5\,HI = 3\,I_2 + 3\,H_2O.$$

In unsaturated compounds, *i.e.*, in those which contain at least two carbon atoms united by a double binding, the halogens dissolve the double binding before substitution takes place. They add on to the molecule:

$$C_2H_4 + Cl_2 = C_2H_4Cl_2, \textit{ i. e.}:$$
$$CH_2{=}CH_2 + Cl_2 = CH_2Cl{-}CH_2Cl$$
$$C_6H_6 + 3\,Cl_2 = C_6H_6Cl_6 \text{ (p. 203).}$$

In the presence of water, the halogens exert an oxidizing action (chlorine, naturally, being the strongest), as they decompose the water, setting free the oxygen, which acts on the organic compound:

$$H_2O + Cl_2 = 2\,HCl + O.$$

2) *Chlor-* and *Bromhydric Acids* replace alcoholic hydroxyls by chlorine or bromine:

$$C_2H_5(OH) + HCl = C_2H_5Cl + H_2O$$

$$\underset{\text{Lactic acid}}{CH_3{-}CH(OH){-}COOH} + HBr = \underset{\text{Brompropionic acid}}{CH_3{-}CHBr{-}COOH} + H_2O$$

$$\text{or } \underset{\text{Ether}}{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}}\!\!>O + 2\,HCl = \begin{matrix}C_2H_5Cl\\C_2H_5Cl\end{matrix} + H_2O.$$

They often dissolve the double binding of unsaturated compounds:

$$CH_2{=}CH_2 + HCl = CH_3{-}CH_2Cl.$$

Iodohydric Acid acts in the same manner, but at an elevated temperature it substitutes inversely, *i. e.*, replaces the substituted haloid by hydrogen :

$$\underset{\text{Iodoacetic acid}}{CH_2I\text{-}COOH} + HI = \underset{\text{Acetic acid}}{CH_3\text{-}COOH} + I_2$$

It acts particularly in this way on oxygen compounds containing hydroxyl, *i.e.*, it reduces them. At a sufficiently high temperature, it produces the saturated hydrocarbon, or it breaks the molecule into molecules of methane :

$$C_3H_8O_3 = \underset{\text{Glycerol}}{CH_2(OH)\text{-}CH(OH)\text{-}CH_2(OH)} + 5\,HI$$

$$= CH_3\text{-}CHI\text{-}CH_3 + 3\,H_2O + 2\,I_2$$

$$\underset{\text{Erythrol}}{C_4H_{10}O_4} + 7\,HI = \underset{\text{Sec. butyl iodide}}{C_4H_9I} + 4\,H_2O + 3\,I_2$$

$$\underset{\text{Amyl alcohol}}{C_5H_{12}O} + 10\,HI = 5\,CH_4 + H_2O + 5\,I_2.$$

As the free iodine in this reaction always acts as a weak oxidizer, it must be at once removed. This is effected by the addition of phosphorus, which unites with the iodine to phosphorus iodide, which is at once decomposed by the water into iodohydric acid (acting again) and phosphorous acid.

3) *Sulphuric Acid* replaces the hydroxyl of the fatty alcohols by HSO_4 ; and the hydrogen of the aromatic hydrocarbons by HSO_3 :

$$\underset{\text{Alcohol}}{C_2H_5(OH)} + HHSO_4 = \underset{\text{Ethylsulphuric acid}}{C_2H_5\text{-}HSO_4} + H_2O.$$

$$C_6H_5H + H(SO_3)OH = \underset{\text{Benzosulphonic acid}}{C_6H_5\text{-}SO_3H} + H_2O.$$

Water is always formed during the reaction. It is produced, either from the hydroxyl of the organic compound and the substitutable hydrogen of the acid, or from the hydrogen of the organic compound and the hydroxyl of the acid.

Sulphuric acid can also substitute both hydroxyls of an alcohol, or two H's of an aromatic compound :

$$2\,C_2H_5OH + H_2SO_4 = \underset{\text{Ethyl sulphate}}{(C_2H_5)_2SO_4} + 2\,H_2O$$

$$2\,C_6H_5H + SO_2(OH)_2 = \underset{\text{Sulphobenzid}}{C_6H_5{}^-SO_2{}^-C_6H_5} + 2\,H_2O.$$

4) *Nitric Acid* forms esters with the alcohols of the fatty series :

$$C_2H_5OH + NO_2(OH) = \underset{\text{Ethyl nitric ester}}{C_2H_5ONO_2} + H_2O$$

$$\underset{\text{Glycerol}}{C_3H_5(OH)_3} + 3\,NO_2(OH) = \underset{\text{Glycerol nitric ester}}{C_3H_5(ONO_2)_3} + 3\,H_2O.$$

With the aromatic compounds it forms substitution-products :

$$C_6H_5H + NO_2(OH) = \underset{\text{Nitrobenzene}}{C_6H_5{}^-NO_2} + H_2O.$$

It acts in the same manner as sulphuric acid, but the different behavior of the two series is here more apparent. With the alcohols of the fatty series, the SO_2 and NO_2 are linked to the hydrocarbon rest by means of oxygen, while with the hydrocarbons of the aromatic series, the binding takes place directly between the nitrogen, or sulphur, and the carbon.

Nitric acid, HO^-NO_2
Sulphuric acid, $HO^-SO_2{}^-OH$
Nitric ethyl ester, $C_2H_5{}^-O^-NO_2$
Ethylsulphuric acid, $C_2H_5{}^-O^-SO_2{}^-OH$
Ethyl sulphate, $C_2H_5{}^-O^-SO_2{}^-O^-C_2H_5$
Nitrobenzene, $C_6H_5{}^-NO_2$
Benzenesulphonic acid, $C_6H_5{}^-SO_2{}^-OH$
Sulphonezid, $C_6H_5{}^-SO_2{}^-C_6H_5$.

Compounds in which the nitrogen of the NO_2-group is bound directly to the carbon are also known in the fatty series, and some of them have been described (p. 105). They

are usually formed by the action of silver nitrite on alkylogens. Sulphonic acids of the fatty series are also known, and are obtained by the action of sulphites on the corresponding haloid derivatives (p. 103).

5) *Potassium and Sodium Hydroxide* decompose the esters when in alcoholic solution:

$$\underset{\text{Acetic ester}}{C_2H_5O\text{-}C_2H_3O} + KOH = \underset{\text{Alcohol}}{C_2H_5OH} + \underset{\text{Potassium acetate}}{C_2H_5KO_2},$$

and change the alkylogens into hydroxyl derivatives:

$$C_2H_5Cl + KOH = C_2H_5OH + KCl.$$

When fused in the solid state with organic bodies, they act as oxidizing agents, substituting oxygen for hydrogen and setting the latter free:

$$C_2H_5OH + KOH = C_2H_3O_2K + 2H_2.$$

Potassium and sodium hydroxides act at a high temperature as very strong bases, producing acids and uniting with them to salts. They convert the aldehydes of the aromatic series into the corresponding alcohols:

$$\underset{\text{Cinnamic aldehyde}}{2\,C_6H_5\text{-}C_3H_3O} + KOH = \underset{\text{Cinnamic acid}}{C_6H_5\text{-}C_3H_2KO_2} + \underset{\text{Cinnamic alcohol}}{C_6H_5\text{-}C_2H_5O}.$$

They often effect the resolution of a complicated molecule into several molecules of simple acids:

$$\underset{\text{Sugar}}{C_6H_{12}O_6} + 6\,NaOH = 3\,C_2Na_2O_4 + 18\,H.$$

The acids derived from hydrocarbons of the C_nH_{2n} series, are decomposed by NaOH and KOH, the molecule breaking at the point where two carbon atoms are united by a double binding:

$$\underset{\text{Potassium crotonate}}{CH_3\text{-}CH{=}CH\text{-}COOK} + KHO + H_2O = CH_3\text{-}COOK + \underset{\text{Potassium acetate}}{CH_3\text{-}COOK} + H_2.$$

6) *Phosphorus Trichloride,* PCl_3, and *Phosphorus Tribromide,* PBr_3, as well as *Phosphorus Oxychloride,* $POCl_3$, and *Bromide,* $POBr_3$, substitute OH by Cl or Br:

$$3\,C_2H_5OH + PCl_3 = 3\,C_2H_5Cl + PH_3O$$
$$3\,C_2H_5(OH) + POBr_3 = 3\,C_2H_5Br + PH_3O_4.$$

7) *Phosphorus Pentachloride,* PCl_5, and *Bromide,* PBr_5, substitute oxygen by Cl_2 or Br_2, acting like free chlorine:

$$\underset{\text{Aldehyde}}{C_2H_4O} + PCl_5 = \underset{\substack{\text{Ethylidene}\\ \text{chloride}}}{C_2H_4Cl_2} + POCl_3.$$

Phosphorus Pentasulphide, P_2S_5, replaces the oxygen of hydroxyl by sulphur:

$$5\,C_2H_5OH + P_2S_5 = 5\,C_2H_5SH + P_2O_5$$
$$5\,CH_3{}^-COOH + P_2S_5 = 5\,CH_3{}^-COSH + P_2O_5.$$

In conclusion we shall mention a phenomenon for which no satisfactory explanation has as yet been offered, viz., the conversion of organic bodies into isomeric ones by *atomic migration.* The formation of urea from ammonium cyanate has been mentioned several times. In ammonium cyanate, the carbon is united to the di-valent oxygen forming the rest CO. The two bonds of the CO are satisfied by the two valences of the N, whose third bond is satisfied by NH_4:

$$O^=C^=N^-NH_4.$$

On boiling with water, the double binding of the N to the C is dissolved to a simple one, and the unsaturated group, $O^=\underset{|}{C}{}^-N^=$, is formed at the moment. In this group, the C has one free bond, and the nitrogen two. One valence of the C takes the N of the NH_4, while two H's of the latter rest satisfy the two bonds of the N which is united to the C, forming the compound, $O^=C\langle^{NH_2}_{NH_2}$, carbamide, or urea.

When glycerol is treated with chlorhydric acid, two bodies

are formed, dichlorhydrins of glycerol, in which two OH's are replaced by Cl's :

$$\begin{array}{ll} CH_2OH\text{-}CHOH\text{-}CH_2OH & \text{Glycerol} \\ CH_2Cl\text{-}CHCl\text{-}CH_2OH \\ CH_2Cl\text{-}CH(OH)\text{-}CH_2Cl & \text{Dichlorhydrin.} \end{array}$$

Both of them yield allyl alcohol with sodium :

$$CH_2Cl\text{-}CHCl\text{-}CH_2(OH) + Na_2 = CH_2{=}CH\text{-}CH_2OH + 2\,NaCl.$$

Hence a shifting, or migration, of the hydroxyl from the middle carbon atom to one of the end carbon atoms must have taken place.

3) Hydrazobenzene, $C_6H_5\text{-}NH{=}NH\text{-}C_6H_5$, is easily transformed by acids into the isomeric benzidine :

$$\begin{array}{l} C_6H_4\text{-}NH_2 \\ C_6H_4\text{-}NH_2 \end{array}$$

Here, again, a rearrangement of the atoms has taken place. The two benzene nuclei have each lost an atom of hydrogen and united with each other, while the binding of the nitrogen atoms has been broken, and the NH has passed into NH_2.

4) By elimination of water the glycol,

$$CH_2(OH)\text{-}CH_2(OH),$$

should pass into ethlylene oxide, $\begin{matrix} CH_2 \\ CH_2 \end{matrix}\!\!>\!O$, but, on the contrary, aldehyde, $CH_3\text{-}CHO$, is formed. Hence an O has become bound by both its valences to a carbon atom, while an H has shifted to another carbon atom.

The secondary and tertiary anilines (methylaniline, dimethylaniline) on heating to 300° are converted into primary bases, toluidine and xylidine :

$C_6H_5NH\text{-}CH_3$, is converted into $C_6H_4(CH_3)NH_2$
$C_6H_5N(CH_3)_2$ " " " $C_6H_3(CH_3)_2NH_2$.

Hence the methyl-group and a hydrogen of the benzene change places. Mellitic acid $C(CO_2H)_6$ is converted into hydromellitic acid, $C_6H_6(CO_2H)_6$, by the action of nascent hydrogen. This latter compound by heating with chlorhydric acid, passes into isohydromellitic acid. In this case, also, it is only possible to explain the reaction by supposing that the atoms, or atomic groups, wander from one carbon atom to another.

There are a great number of bodies which are converted into isomeric compounds at an elevated temperature, but we have not space to mention them.

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